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## **Application For Letters Patent Of The United States**

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Title of Invention:

SILVER SALT PHOTOTHERMOGRAPHIC DRY IMAGING MATERIAL

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To All Whom It May Concern:  
The following is a specification  
of the aforesaid Invention:

## **SILVER SALT PHOTOTHERMOGRAPHIC DRY IMAGING MATERIAL**

### **FIELD OF THE INVENTION**

The present invention relates to a silver salt photothermographic dry imaging material and an image recording method and a imaging method by the use thereof.

### **BACKGROUND OF THE INVENTION**

In the field of medical diagnosis and graphic arts, there has been desired techniques relating to a photothermographic material in which efficient light-exposure is feasible as is done in a laser imager or laser image setter and by which definite, clear black images are obtained.

As a technique described above, a thermal imaging system employing organic silver salts is described, for example, in U.S. Patents 3,152,904 and 3,487,075; D. Morgan,

Dry Silver Photographic Material; and D.H. Klosterboer, "Thermally Processed Silver Systems" in IMAGING PROCESSES and MATERIALS, Neblette's Eighth Edition, edited by J.M. Sturge, V. Walworth, and A. Shepp (1969) page 279. Specifically, a silver salt photothermographic dry imaging material contains a reducible light-insensitive silver source (such as organic silver salts), a catalytically active amount of photocatalyst (such as silver halide) and a reducing agent, which are dispersed in a binder matrix. Such a photothermographic material is stable at ordinary temperature and, after exposure, form silver upon heating at a relatively high temperature (e.g., 80° C or higher) through an oxidation reduction reaction between the reducible silver source (which functions as an oxidizing agent) and the reducing agent. The oxidation reduction reaction is accelerated by catalytic action of a latent image produced by the exposure. Silver formed through reaction of the reducible silver salt in exposed areas provides a black image, which contrasts with non-exposed areas, leading to image formation. The foregoing photothermographic material is also disclosed in literature, for example, U.S. Patent No. 2,910,377 and JP-B No. 43-4924 (hereinafter, the term, JP-B refers to Japanese Patent Publication).

The silver salt photothermographic dry imaging material (which is hereinafter also denoted simply as photothermographic material) has often been used in medical diagnosis from its convenience. Fine representation is desired as medical diagnostic imaging so that high image quality with superior sharpness and enhanced graininess is required and blue black tone images tend to be favored in terms of easiness in diagnosis. However, it is rather difficult to produce neutral black image tone in such a photothermographic imaging system employing organic silver salts, so that image tone is modified using image toning agents, but such tone control is not sufficient to obtain an intended image and an improvement is still desired.

There was disclosed a technique to improve such a drawback, in which a specific reducing agent is used in combination with a specific compound, as described in JP-A No. 2002-169246 (hereinafter, the term, JP-A refers to Japanese Patent Application Publication). However, it was hard to say that images obtained in such a technique were a satisfactory image quality level for use in medical diagnosis. Thus, image color or density is easily changed by the action of light or heat during storage, producing relatively high fog density and low maximum density and



resulting in serious inferior such that when exposed using a laser scanning exposure machine, the output image density significantly varies in response to a slight fluctuation in oscillation wavelength. Therefore, a further improvement is desired.

#### **SUMMARY OF THE INVENTION**

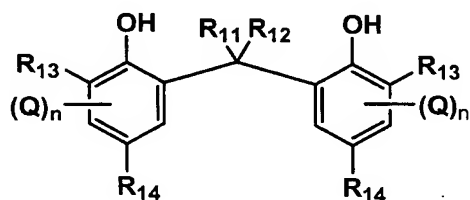
Accordingly, it is an object of the present invention to provide a silver salt photothermographic dry imaging material producing silver images of blue black tone, in which image color or density and background density are hard to be deteriorated by influences of light or heat during storage, exhibiting enhanced sensitivity and maximum density as well as minimized fog density and resulting in superior stability in sensitivity and maximum density of output images for variation in oscillation wavelength when exposed using a laser scanning exposure machine.

The foregoing object can be accomplished by the following constitution:

1. A silver salt photothermographic dry imaging material comprising on a support a light-sensitive layer comprising a light-sensitive emulsion containing light-insensitive organic silver salt grains and light-sensitive

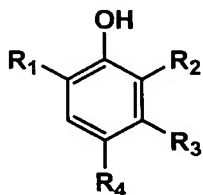
silver halide grains, a reducing agent for silver ions and a binder, wherein the reducing agent for silver ions is a compound represented by the following formula (1) and the light-sensitive layer further comprises a hindered phenol compound represented by the following formula (2):

formula (1)



wherein R<sub>11</sub> and R<sub>12</sub> are each a hydrogen atom, a 3- to 10-membered non-aromatic ring group or a 5- or 6-membered aromatic ring group, provided that R<sub>11</sub> and R<sub>12</sub> are not hydrogen atoms at the same time; R<sub>13</sub> and R<sub>14</sub> are each a hydrogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an aryl group or a heterocyclic group; Q is a group capable of being substituted on a benzene ring; n is 0, 1 or 2, provided that when n is 2, two Qs may be the same with or different from each other;

formula (2)



wherein  $R_1$  is an alkyl group or a cycloalkyl group;  $R_2$  is a hydrogen atom, an alkyl group, a cycloalkyl group, or an acylamino group;  $R_3$  is a hydrogen atom, an alkyl group or a cycloalkyl group;  $R_4$  is a group capable of being substituted on a benzene ring.

#### DETAILED DESCRIPTION OF THE INVENTION

One aspect of this invention is directed to a silver salt photothermographic dry imaging material comprising on a support a light-sensitive layer comprising a light-sensitive emulsion containing light-insensitive organic silver salt grains and light-sensitive silver halide grains, a reducing agent for silver ions, a hindered phenol and a binder, wherein the reducing agent for silver ions is a compound represented by the foregoing formula (1) and the hindered phenol is a compound represented by the foregoing formula (2).

First, the compound represented by the formula (1) will be described. In the formula (1),  $R_{11}$  and  $R_{12}$  are each a hydrogen atom, a 3- to 10-membered non-aromatic ring group or a 5- or 6-membered aromatic ring group. Of the 3- to 10-membered non-aromatic ring groups represented by  $R_{11}$  and  $R_{12}$ , 3-membered non-aromatic ring groups include, for example,

cyclopropyl, aziridyl and oxiranyl; 4-membered ring groups include cyclobutyl, cyclobutenyl, oxetanyl and azetidiny; 5-membered ring groups include cyclopentyl, cyclopentenyl, cyclopentadienyl, tetrahydrofuranyl, pyrrolidiny and tetrahydrothienyl; 6-membered ring groups include cyclohexyl, cyclohexenyl, cyclohexadienyl, tetrahydropiranyl, piperidiny, dioxanyl, tetrahydrothiopyranyl, norcaranyl, norpiranyl and norbornyl; 7-membered ring groups include cycloheptyl, cycloheptenyl and cycloheptadienyl; 8-membered ring groups include cyclooctanyl, cyclooctenyl, cyclooctadienyl and cyclooctatrienyl; 9-membered ring groups include cyclononanyl, cyclononenyl, cyclononadienyl and cyclononatrienyl; 10-membered ring groups include cyclodecanyl, cyclodecenyl, cyclodecadienyl and cyclodecatrienyl.

Of the foregoing 3- to 10-membered ring groups, 3- to 6-membered ring groups are preferred, 5- and 6-membered ring groups are more preferred, and a 6-membered ring group is still more preferred. Further, of the foregoing ring groups, hydrocarbon rings, which contain no heteroatom, are specifically preferred. These rings may form a spiro-bonding through a spiro atom or may be condensed with other rings including an aromatic ring. The foregoing ring groups may be

substituted. Examples of substituent groups include a halogen atom (e.g., fluorine, chlorine, bromine), cycloalkyl group (e.g., cyclohexyl, cycloheptyl), cycloalkenyl group (e.g., 1-cycloalkenyl, 2-cycloalkenyl), alkoxy group (e.g., methoxy, ethoxy, propoxy), alkylcarbonyloxy group (e.g., acetyloxy), alkylthio group (e.g., methylthio, trifluoromethylthio), carboxyl group, alkylcarbonylamino group (e.g., acetylamino), ureido group (e.g., methylaminocarbonylamino), alkylsulfonyl group (e.g., methanesulfonyl, trifluoromethanesulfonyl), carbamoyl group (e.g., carbamoyl, N,N-dimethylcarbamoyl, N-morpholinocarbonyl), sulfamoyl group (e.g., sulfamoyl, N,N-dimethylsulfamoyl, morpholinosulfamoyl), trifluoromethyl, hydroxy, nitro, cyano, alkylsulfonamido group (e.g., methanesulfonamido, butanesulfoneamido), alkylamino group (e.g., N,N-dimethylamino, N,N-diethylamino), sulfo group, phosphono group, sulfite group, sulfinio group, alkylsulfonylaminocarbonyl group (e.g., methanesulfonylaminocarbonyl, ethanesulfonylaminocarbonyl), alkylcarbonylaminosulfonyl group (e.g., acetoamidossulfonyl, methoxyacetoamidossulfonyl), alkynylaminocarbonyl group (e.g., acetoamidocarbonyl, methoxyacetoamidocarbonyl), and alkylsulfinylaminocarbonyl group (e.g.,

methanesulfinylaminocarbonyl, ethane sulfinylaminocarbonyl). In the case of being substituted by plural substituents, the plural substituents may be the same or different. Of the foregoing substituent groups, an alkyl group is specifically preferred.

The 5- or 6-membered aromatic ring group designated by  $R_{11}$  and  $R_{12}$  may be a monocyclic group or a condensed ring group, and is preferably a monocyclic or bicyclic aromatic carbon ring (e.g., benzene ring, naphthalene ring), and more preferably a benzene ring. An aromatic heterocycle is preferably a 5- or 6-membered aromatic heterocycle, and more preferably a 5-membered aromatic heterocycle, which may be condensed with other rings. Examples of preferred heterocycles include imidazole, pyrazole, thiophene, furan, pyrrole, pyridine, pyrimidine, pyrazine, pyridazine, triazole, triazine, indole, indazole, purine, thiadiazole, oxadiazole, quinoline, phthalazine, naphthyridine, quinoxaline, quinazolinone, cinnoline, pteridine, acridine, phenanthroline, phenazine, tetrazole, thiazole, oxazole, benzimidazole, benzoxazole, benzthiazole, indolenine and tetrazaindene; and imidazole, pyrazole, thiophene, furan, pyrrole, triazole, thiadiazole, tetrazole, thiazole, benzimidazole, and benzthiazole are more preferred. The

foregoing rings may be condensed with other rings, on which any substituent may be substituted. Examples of such substituents are the same as described in the foregoing 3- to 10-membered non-aromatic ring groups. Most preferred combination of  $R_{11}$  and  $R_{12}$  is  $R_{11}$  of a 5-membered aromatic heterocyclic group and  $R_{12}$  of a hydrogen atom.

$R_{13}$  and  $R_{14}$  are each a hydrogen atom, an alkyl group, cycloalkyl group, alkenyl group, cycloalkenyl group, aryl group or heterocyclic group. The alkyl group is preferably one having 1 to 10 carbon atoms. Examples thereof include methyl, ethyl, propyl, iso-propyl, butyl, t-butyl, pentyl, iso-pentyl, 2-ethyl-hexyl, octyl, decyl, cyclohexyl, cyclopropyl, 1-methylcyclohexyl, ethenyl-2-propenyl, 3-butenyl, 1-methyl-3-propenyl, 3-pentenyl, 1-methyl-3-butenyl, 1-cycloalkenyl group, 2-cycloalkenyl group, ethynyl and 1-propynyl.  $R_{13}$  is preferably an alkyl group or cycloalkyl group, such as methyl, ethyl, iso-propyl, t-butyl, cyclohexyl, and 1-methylcyclohexyl, more preferably a primary alkyl group such as methyl or a tertiary alkyl group such as t-butyl, and 1-methylcyclohexyl, and still more preferably a tertiary alkyl group such as t-butyl and 1-methylcyclohexyl.  $R_{14}$  is preferably an alkyl or cycloalkyl group such as methyl, ethyl, iso-propyl, t-butyl, cyclohexyl, 1-

methylcyclohexyl, and 2-hydroxyethyl, more preferably a primary alkyl group, and still more preferably methyl or 2-hydroxyethyl. Examples of an aryl group represented by  $R_{13}$  and  $R_{14}$  include phenyl, naphthyl and anthranyl group. Examples of a heterocyclic group represented by  $R_{13}$  and  $R_{14}$  include aromatic heterocyclic groups such as a pyridine group, quinoline group, isoquinoline group, imidazole group, pyrazole group, triazole group, oxazole group, thiazole group, oxadiazole group, thiadiazole group, and tetrazole group, and non-aromatic heterocyclic groups such as piperidino, morpholino, tetrahydrofuryl, tetrahydrothienyl and tetrahydropyranyl groups. These groups may be substituted, and substituents are the same as described above. The most preferable combination of  $R_{13}$  of a tertiary alkyl group (e.g., t-butyl, 1-methylcyclohexyl) and  $R_{14}$  of a primary alkyl group (e.g., methyl, 2-hydroxyethyl) is most preferred.

Q is a group capable of being substituted on a benzene ring. Specific example thereof include an alkyl group having 1 to 25 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, t-butyl, pentyl), halogenated alkyl group (e.g., trifluoromethyl, perfluorooctyl), cycloalkyl group (e.g., cyclohexyl, cyclopentyl), alkynyl group (e.g., propargyl),

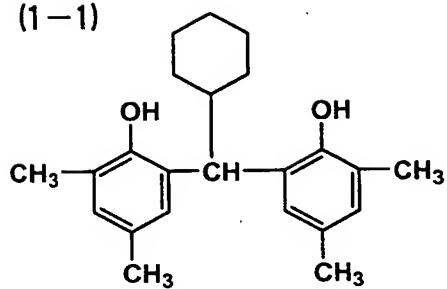


glycidyl group, acrylate group, methacrylate group, aryl group (e.g., phenyl), heterocyclic group (pyridyl, thiazolyl, pyrimidyl, pyridadiny, selenazolyl, sulfolanyl, piperidiny, pyrazolinyl, pyrazolyl, tetrazolyl), halogen atom (e.g., chlorine, bromine, iodine, fluorine), alkoxy group (e.g., methoxy, ethoxy, propyloxy, pentyloxy, cyclopentyloxy, hexyloxy, cyclohexyloxy), aryloxy group (e.g., phenoxy), alkoxy carbonyl group (e.g., methyloxycarbonyl, ethyloxycarbonyl, butyloxycarbonyl), aryloxycarbonyl group (e.g., phenyloxycarbonyl), sulfoneamido group (e.g., methanesulfoneamido, ethanesulfoneamido, butanesulfoneamido, hexanesulfoneamido, cyclohexanesulfoneamido, benzenesulfoneamido), sulfamoyl group (e.g., aminosulfonyl, methylaminosulfonyl, dimethylaminosulfonyl, butylaminosulfonyl, hexylaminosulfonyl, cyclohexylaminosulfonyl, phenylaminosulfonyl, 2-pyridylaminosulfonyl), urethane group (e.g., methylureido, ethylureido, pentylureido, cyclohexylureido, phenylureido, 2-pyridylureido), acyl group (e.g., acetyl, propionyl, butanoyl, hexanoyl, cyclohexanoyl, benzoyl, pyridinoyl), carbamoyl group (e.g., aminocarbonyl, methylaminocarbonyl, dimethylaminocarbonyl, propylaminocarbonyl, pentylaminocarbonyl, cyclohexylaminocarbonyl,

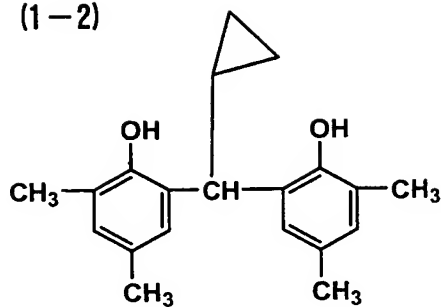
phenylamionocarbonyl, 2-pyridylaminocarbonyl), amido group (e.g., acetoamide, propionamide, butanamide, hexanamide, benzamide), sulfonyl group (e.g., methylsulfinyl, ethylsulfinyl, butylsulfonyl, cyclohexylsulfonyl, phenylsulfinyl, 2-pyridylsulfonyl), amino group (e.g., amino, ethylamino, dimethylamino, butylamino, cyclopentylamino, anilino, 2-pyridylamino), cyano, nitro, sulfo, carboxyl, hydroxy, and oxamoyl. These groups may further be substituted by the foregoing group. In the formula, n is 0, 1 or 2, and preferably 0. Plural Qs may be the same or different.

Specific examples of the reducing agent for silver ions, represented by formula (1) are shown below but are by no means limited to these.

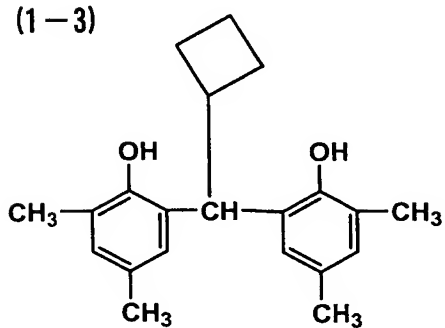
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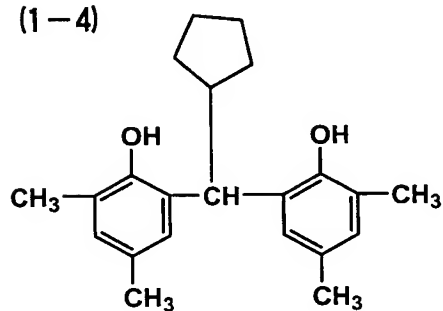
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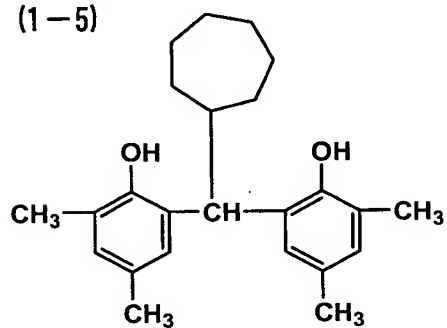
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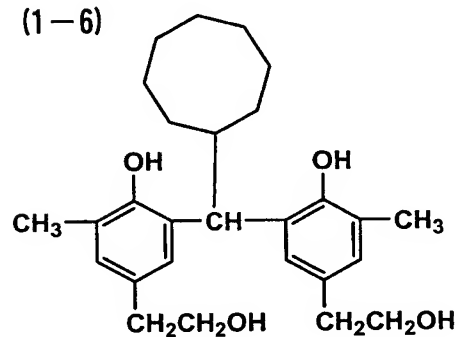
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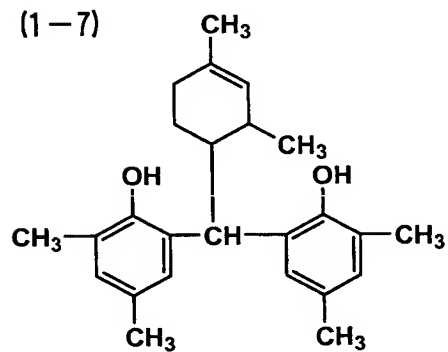
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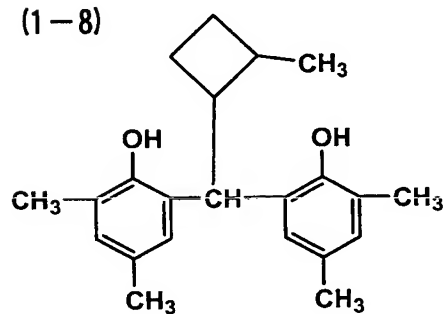
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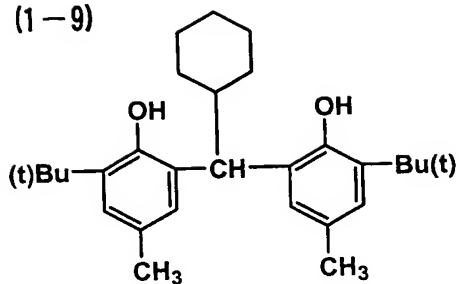
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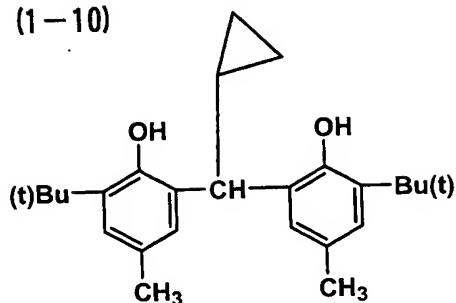
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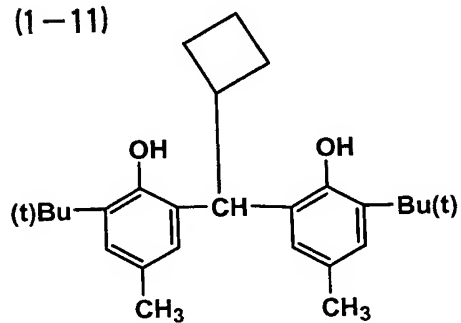
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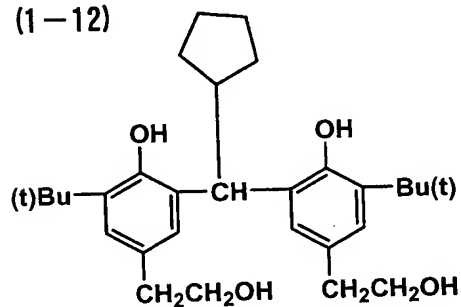
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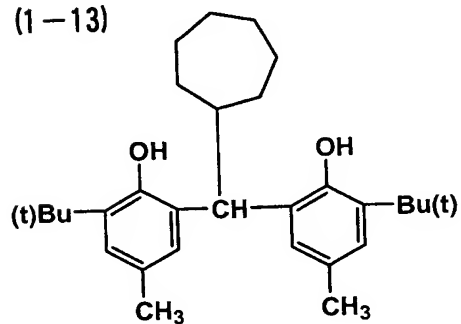
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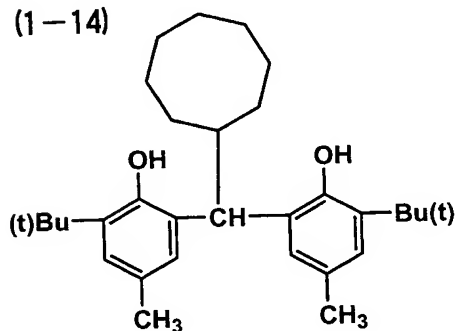
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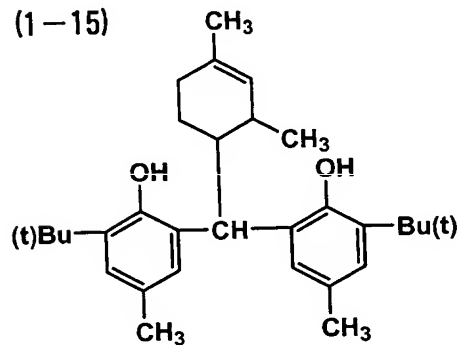
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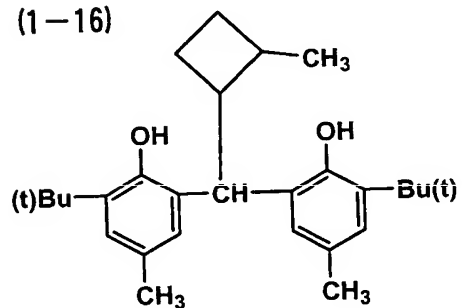
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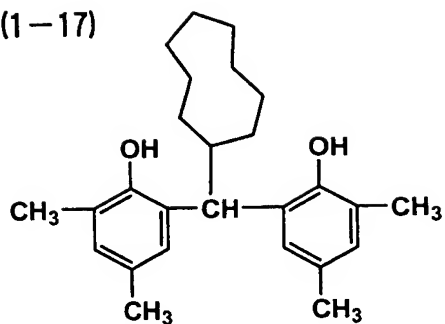
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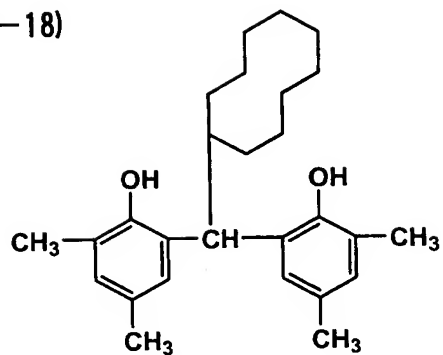
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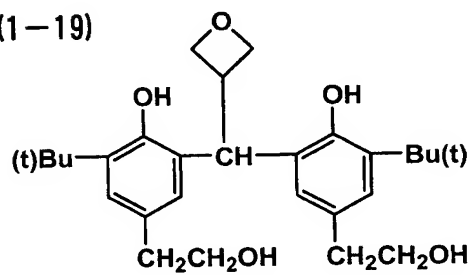
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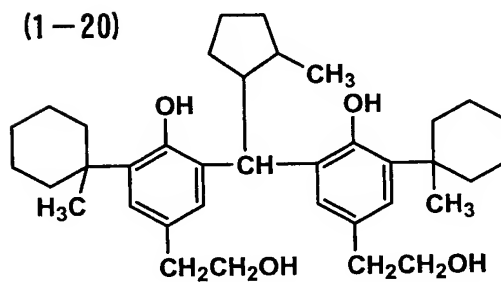
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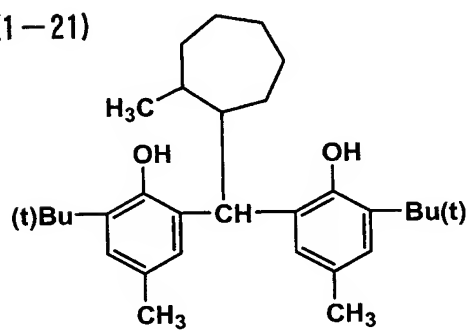
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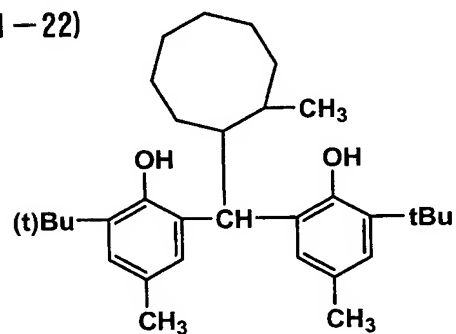
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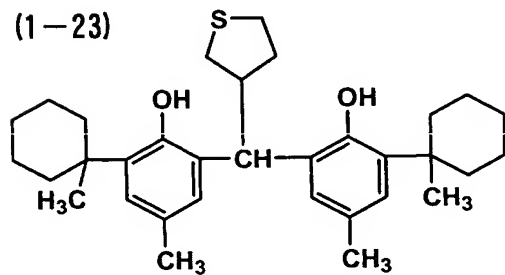
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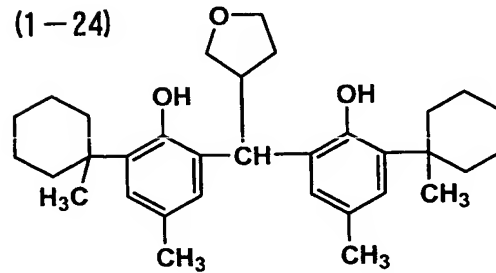
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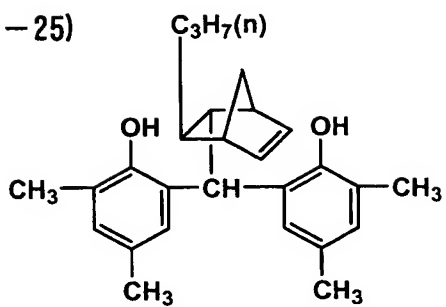
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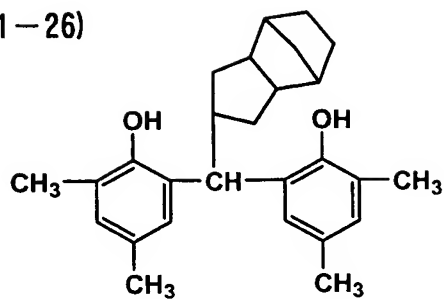
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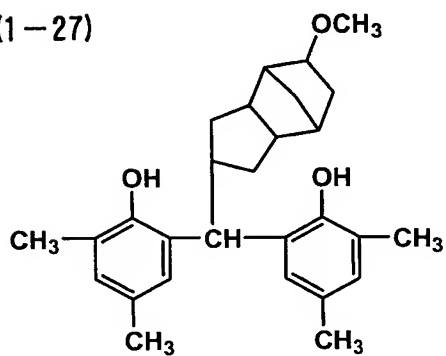
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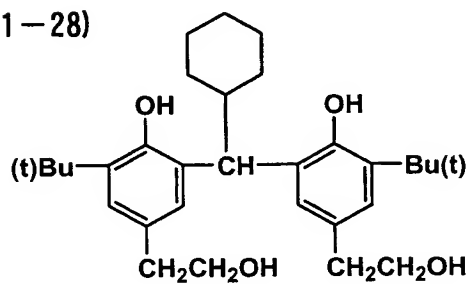
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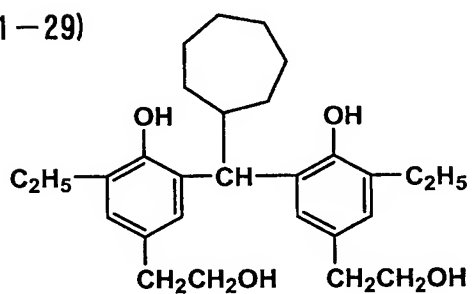
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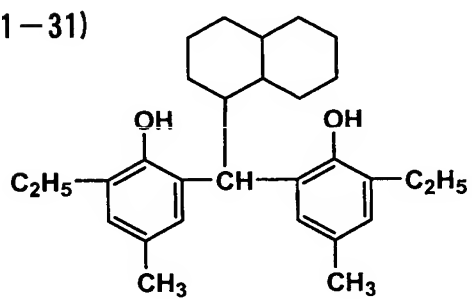
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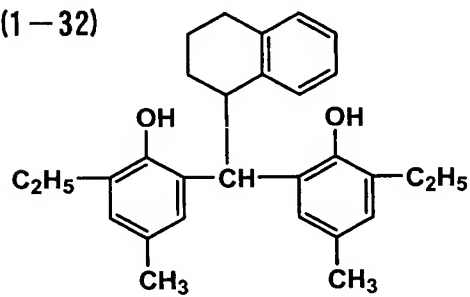
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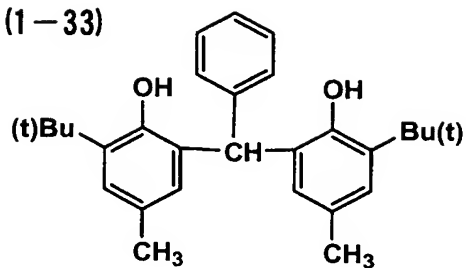
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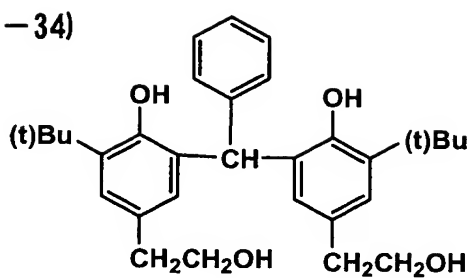
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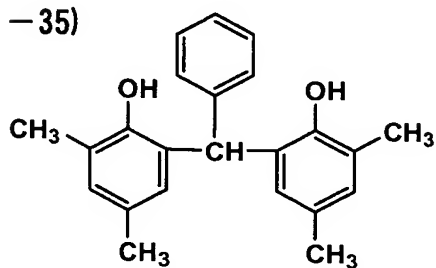
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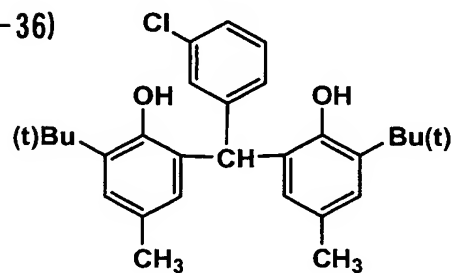
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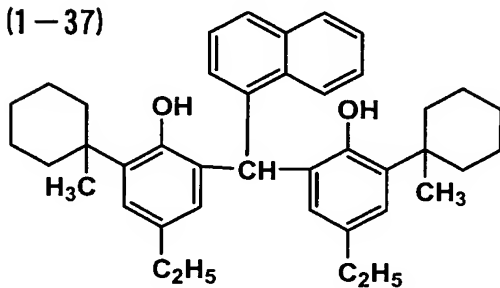
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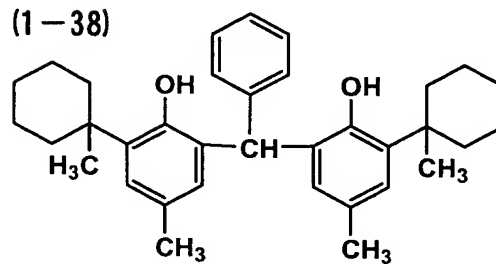
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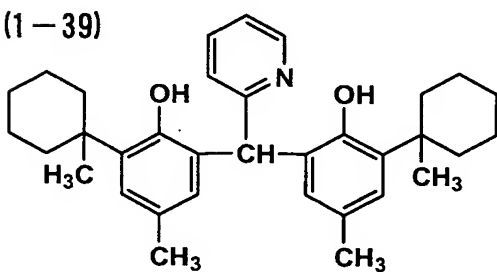
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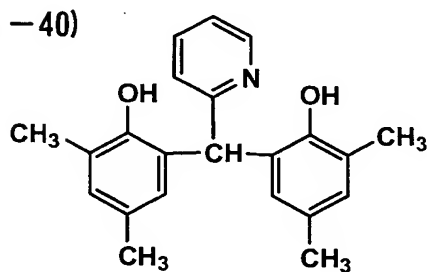
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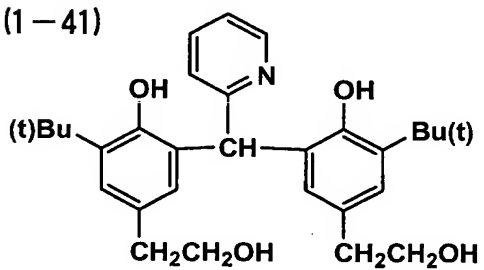
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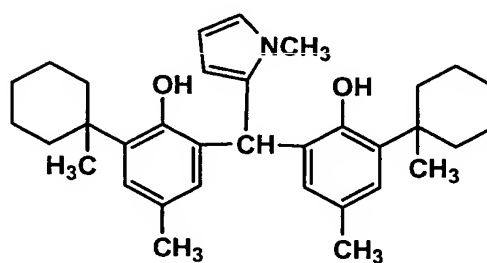
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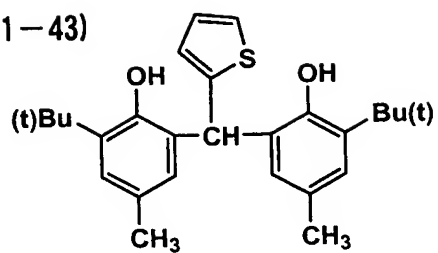
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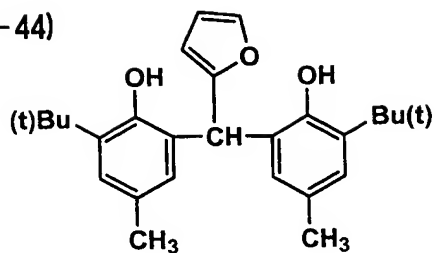
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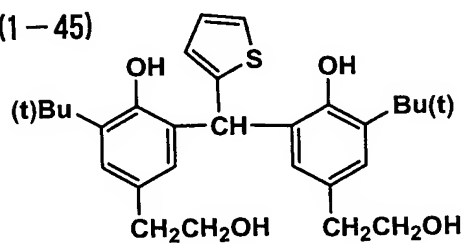
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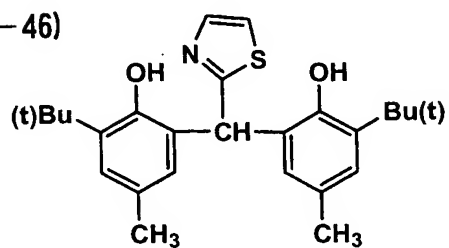
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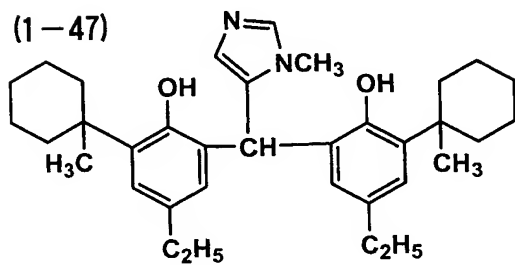
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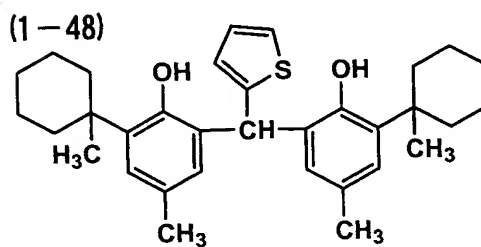
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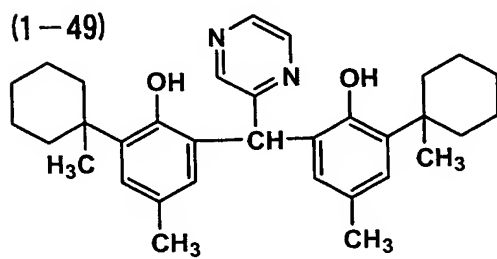
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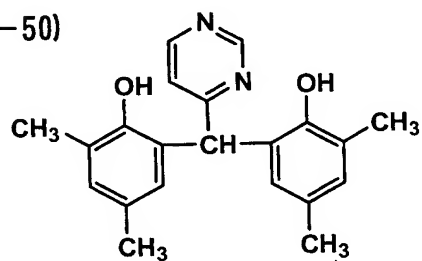
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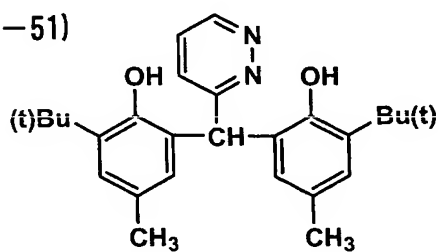
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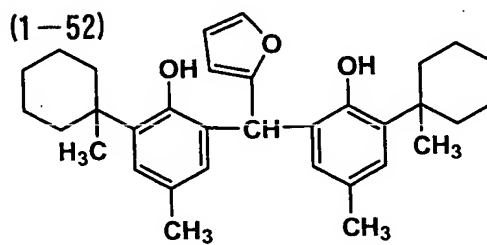
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(1-51)

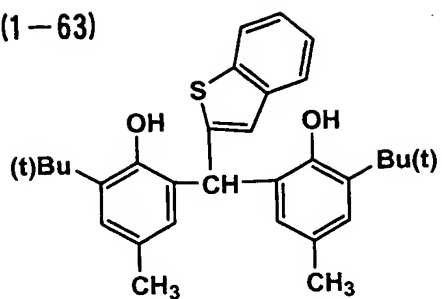


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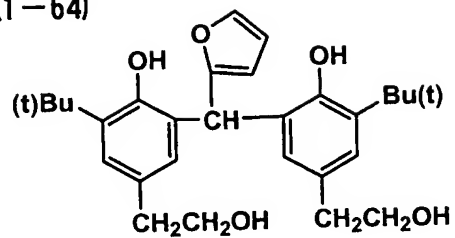




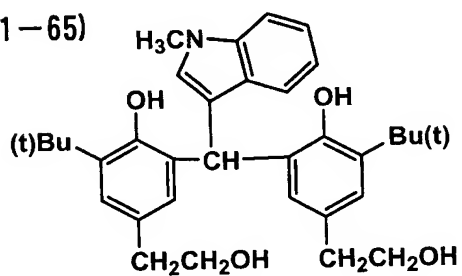
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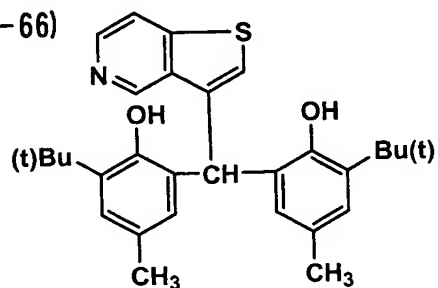
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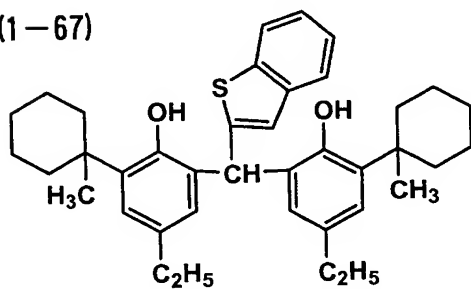
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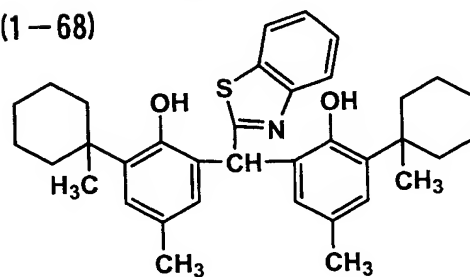
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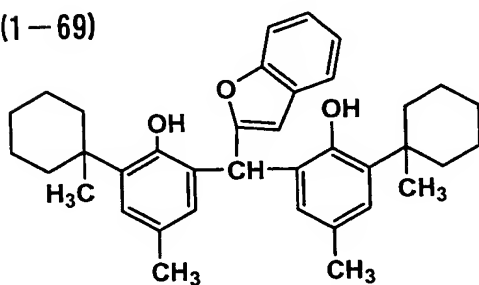
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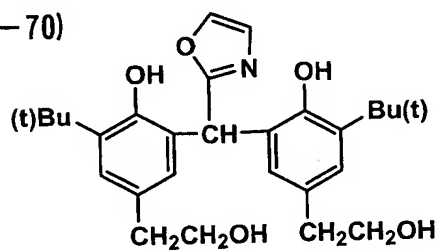
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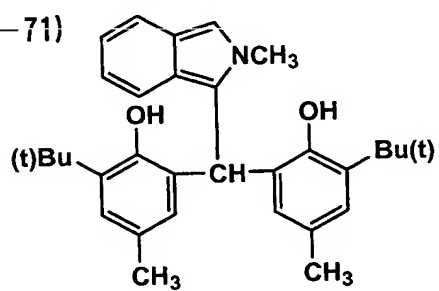
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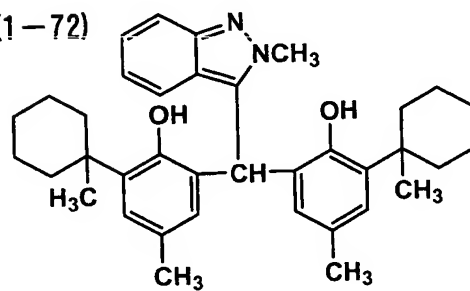
(1-70)



(1-71)



(1-72)



The amount of a reducing agent for silver ions to be used in the photothermographic materials relating to this invention, depending on the kind of organic silver salts, reducing agent, or other additives is usually 0.05 to 10 mol, and preferably 0.1 to 3 mol per mol of organic silver salt. Two or more reducing agents may be used in combination, in an amount within the foregoing range. Addition of the reducing agent to a light sensitive emulsion comprising a light sensitive silver halide, organic silver salt grains and a solvent immediately before coating the emulsion is often preferred, thereby minimizing variation in photographic performance during standing.

The hindered phenol compound represented by the foregoing formula (2) is further described. In the formula (2),  $R_1$  represents a substituted or unsubstituted alkyl or cycloalkyl group. In cases where  $R_2$  is a group other than a hydrogen atom,  $R_1$  is a substituted or unsubstituted alkyl or cycloalkyl group. The alkyl group is preferably one having 1 to 30 carbon atoms, and examples of unsubstituted alkyl or cycloalkyl group include methyl, ethyl, butyl, octyl, isopropyl, t-butyl, t-octyl, t-amyl, sec-butyl, cyclohexyl, and 1-methylcyclohexyl. Of these, groups which are sterically larger (or more bulky) than isopropyl group, such as

isopropyl, iso-nonyl, t-butyl, t-amyl, t-octyl, cyclohexyl, 1-methyl-cyclohexyl and adamantly are preferred, and a tertiary alkyl group, such as t-butyl, t-octyl and t-amyl is more preferred. In cases where  $R_1$  is substituted, substituent thereof include, for example, a halogen atom, aryl group, alkoxy group, amino group, acyl group, acylamino group, alkylthio group, arylthio group, sulfonamido group, acyloxy group, oxycarbonyl group, carbamoyl group, sulfamoyl group, sulfonyl group, and phosphoryl group.

$R_2$  is a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted acylamino group.  $R_2$  is preferably an alkyl group having 1 to 30 carbon atoms or acylamino group having 1 to 30 carbon atoms. Examples of the alkyl or cycloalkyl group include the same as cited in the foregoing  $R_1$ . The acylamino group, which may be unsubstituted or substituted include, for example, acetylamino group, alkoxyacetylamino group and aryloxyacetylamino group.  $R_2$  is preferably a hydrogen atom or an unsubstituted alkyl group having 1 to 24 carbon atoms, such as methyl, isopropyl, or t-butyl.

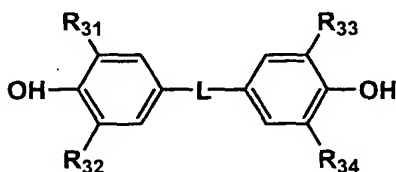
$R_3$  is a hydrogen atom, or a substituted or unsubstituted alkyl or cycloalkyl group.  $R_3$  is preferably an alkyl group having 1 to 30 carbon atoms, and examples of the

alkyl or cycloalkyl group include those as cited in the foregoing R<sub>1</sub>. R<sub>3</sub> is preferably a hydrogen atom or unsubstituted alkyl or cycloalkyl group having 1 to 24 carbon atoms, and examples thereof include methyl, isopropyl and t-butyl. One of R<sub>2</sub> and R<sub>3</sub> is preferably a hydrogen atom.

R<sub>4</sub> is a group capable of being substituted on a benzene ring, and examples thereof include those as cited in the foregoing Q in the formula (1). R<sub>4</sub> is preferably substituted or unsubstituted alkyl or cycloalkyl group having 1 to 30 carbon atoms or an oxycarbonyl group having 2 to 30 carbon atoms, and more preferably an alkyl or cycloalkyl group having 1 to 24 carbon atoms. Substituents for the alkyl or cycloalkyl group include, for example, an aryl group, amino group, alkoxy group, oxycarbonyl group, acylamino group, imido group and ureido group. Of these, an aryl group, amino group, oxycarbonyl group and alkoxy group are preferred. These group may further be substituted.

The compound represented by formula (2) is preferably a compound represented by the following formula (3):

formula (3)

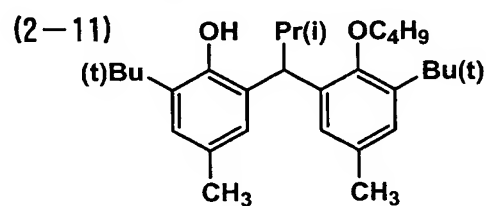
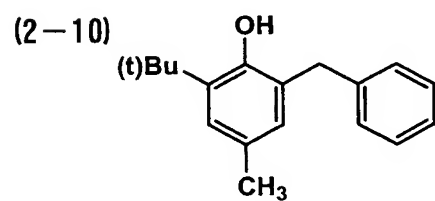
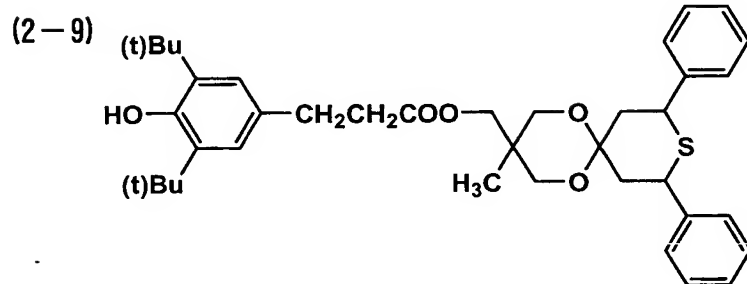
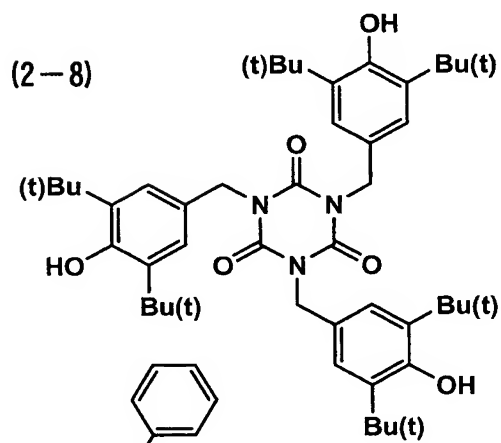
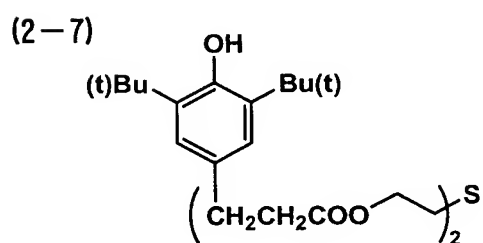
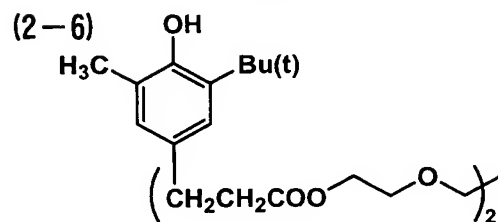
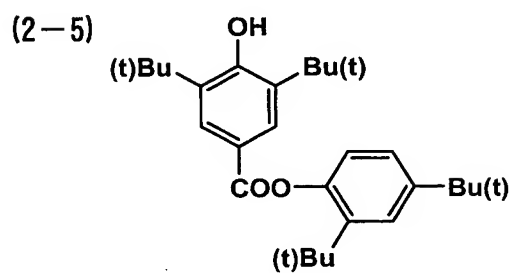
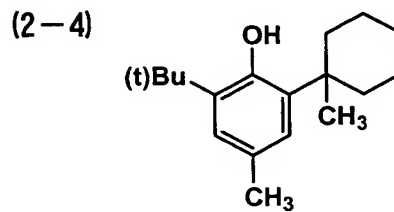
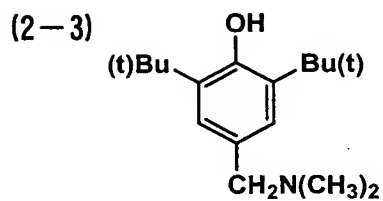
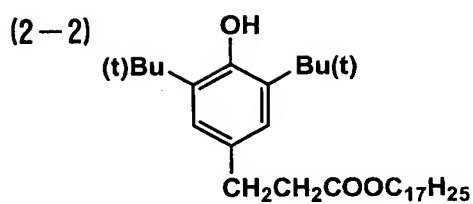
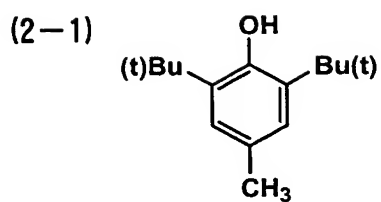


wherein  $R_{31}$ ,  $R_{32}$ ,  $R_{33}$  and  $R_{34}$  are each an alkyl or cycloalkyl group (preferably having 1 to 20 carbon atoms); L is -S- or -CHR<sub>35</sub>, in which  $R_{35}$  is a hydrogen atom, or a substituted or unsubstituted alkyl or cycloalkyl group (preferably having 1 to 20 carbon atoms). In the formula, the alkyl or cycloalkyl group represented by  $R_{31}$ ,  $R_{32}$ ,  $R_{33}$  and  $R_{34}$  may be substituted, and examples of substituents thereof include an aryl group, hydroxy group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acylamino group, sulfonamido group, sulfonyl group, phosphoryl group, acyl group, carbamoyl group, ester group and a halogen atom. At least one of  $R_{31}$ ,  $R_{32}$ ,  $R_{33}$  and  $R_{34}$  is preferably a group which is sterically larger (or more bulky) than isopropyl group, such as isopropyl, isononyl, t-butyl, t-amyl, t-octyl, cyclohexyl, 1-methyl-cyclohexyl and adamantly, and at least two are more preferably such groups. As the foregoing sterically larger group than isopropyl is specifically preferred t-butyl, t-octyl and t-amyl.

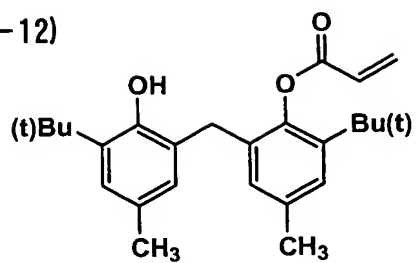
In the formula (3), L is -S- or -CHR<sub>35</sub>-, in which  $R_{35}$  is a hydrogen atom or a substituted or unsubstituted alkyl or cycloalkyl group having 1 to 20 carbon atoms, preferably a hydrogen atom or a substituted or unsubstituted alkyl or cycloalkyl group having 1 to 15 carbon atoms (such as methyl,

ethyl, propyl, isopropyl and 2,4,4-trimethylpentyl).  $R_{35}$  is more preferably a hydrogen atom.

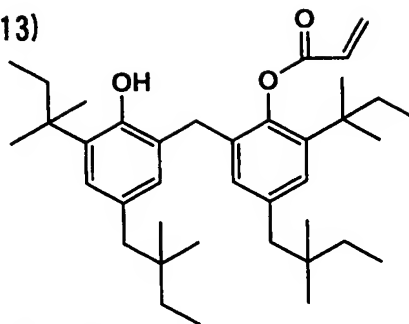
Specific examples of the hindered phenol compounds represented by formulas (2) and (3) are shown below but are not limited to these.



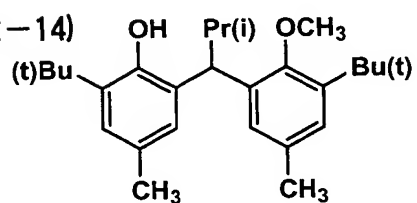
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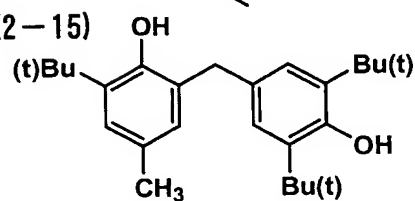
(2-13)



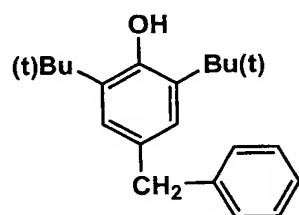
(2-14)



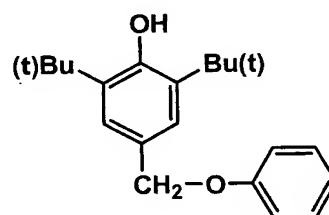
(2-15)



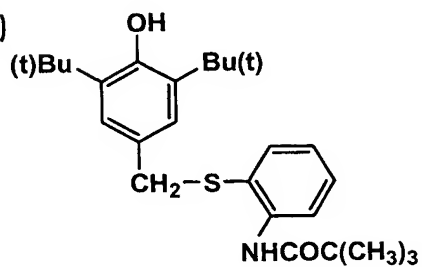
(2-16)



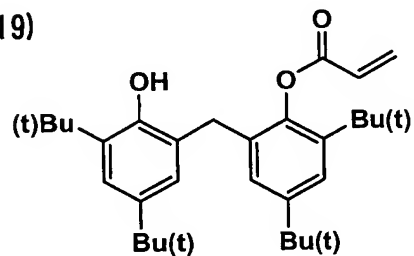
(2-17)



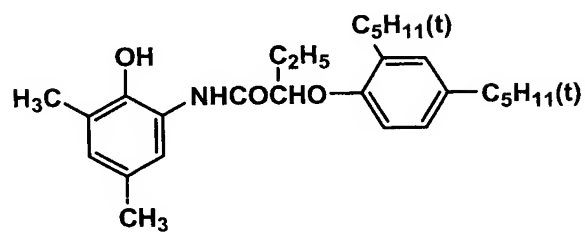
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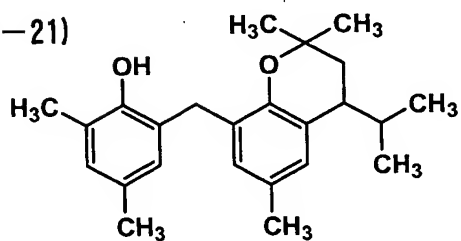
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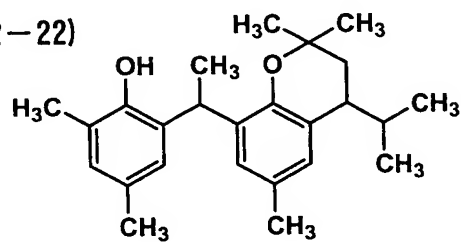
(2-20)



(2-21)

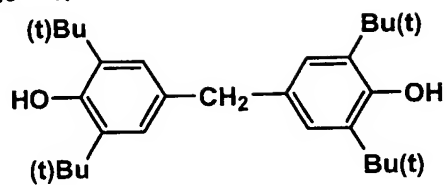


(2-22)

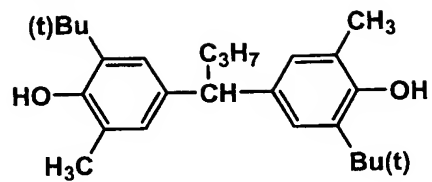




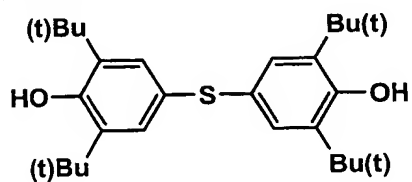
(3-1)



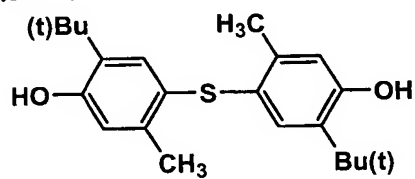
(3-2)



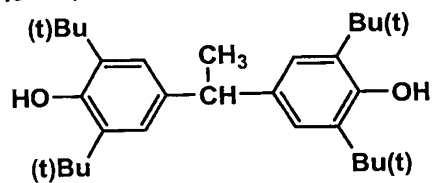
(3-3)



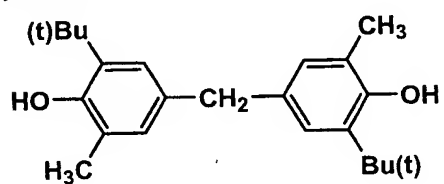
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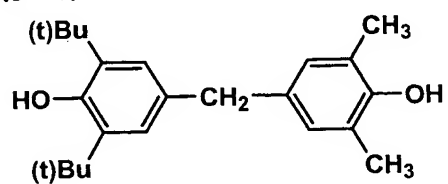
(3-5)



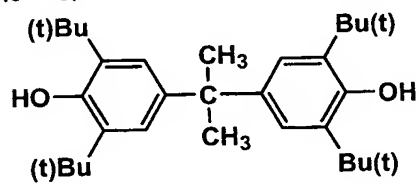
(3-6)



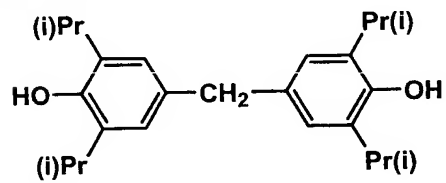
(3-7)



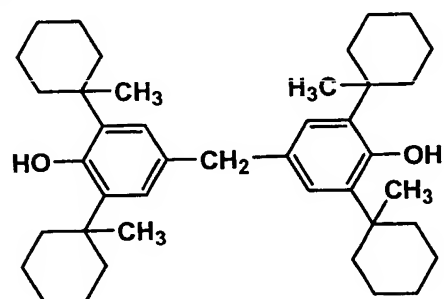
(3-8)



(3-9)



(3-10)



Light-sensitive silver halide grains used in this invention are those which are capable of absorbing light as an inherent property of silver halide crystal or capable of absorbing visible or infrared light by artificial physico-chemical methods, and which are treated or prepared so as to cause a physico-chemical change in the interior and/or on the surface of the silver halide crystal upon absorbing light within the region of ultraviolet to infrared.

The silver halide grains used in the invention can be prepared according to the methods described in P. Glafkides, *Chimie Physique Photographique* (published by Paul Montel Corp., 19679; G.F. Duffin, *Photographic Emulsion Chemistry* (published by Focal Press, 1966); V.L. Zelikman et al., *Making and Coating of Photographic Emulsion* (published by Focal Press, 1964). Any one of acidic precipitation, neutral precipitation and ammoniacal precipitation is applicable and the reaction mode of aqueous soluble silver salt and halide salt includes single jet addition, double jet addition and a combination thereof. Specifically, preparation of silver halide grains with controlling the grain formation condition, so-called controlled double-jet precipitation is preferred. The halide composition of silver halide is not specifically limited and may be any one of silver chloride, silver

chlorobromide, silver iodochlorobromide, silver bromide, silver iodobromide and silver iodide.

The grain forming process is usually classified into two stages of formation of silver halide seed crystal grains (nucleation) and grain growth. These stages may continuously be conducted, or the nucleation (seed grain formation) and grain growth may be separately performed. The controlled double-jet precipitation, in which grain formation is undergone with controlling grain forming conditions such as  $pAg$  and  $pH$ , is preferred to control the grain form or grain size. In cases when nucleation and grain growth are separately conducted, for example, a soluble silver salt and a soluble halide salt are homogeneously and promptly mixed in an aqueous gelatin solution to form nucleus grains (seed grains), thereafter, grain growth is performed by supplying soluble silver and halide salts, while being controlled at a  $pAg$  and  $pH$  to prepare silver halide grains. After completing the grain formation, the resulting silver halide grain emulsion is subjected to desalting to remove soluble salts by commonly known washing methods such as a noodle washing method, a flocculation method, a ultrafiltration method, or electrodialysis to obtain desired emulsion grains.

In order to minimize cloudiness after image formation and to obtain excellent image quality, the less the average grain size, the more preferred, and the average grain size is preferably not more than 0.2  $\mu\text{m}$ , more preferably between 0.01 and 0.17  $\mu\text{m}$ , and still more preferably between 0.02 and 0.14  $\mu\text{m}$ . The average grain size as described herein is defined as an average edge length of silver halide grains, in cases where they are so-called regular crystals in the form of cube or octahedron. Furthermore, in cases where grains are tabular grains, the grain size refers to the diameter of a circle having the same area as the projected area of the major faces. Furthermore, silver halide grains are preferably monodisperse grains. The monodisperse grains as described herein refer to grains having a coefficient of variation of grain size obtained by the formula described below of not more than 30%; more preferably not more than 20%, still more preferably not more than 3%, and most preferably not more than 15%:

$$\begin{aligned} &\text{Coefficient of variation of grain size} = \text{standard} \\ &\text{deviation of grain diameter/average grain diameter} \times \\ &100(\%) \end{aligned}$$

The grain form can be of almost any one, including cubic, octahedral or tetradecehedral grains, tabular grains, spherical grains, bar-like grains, and potato-shaped grains. Of these, cubic grains, octahedral grains, tetradecehedral grains and tabular grains are specifically preferred.

The aspect ratio of tabular grains is preferably 1.5 to 100, and more preferably 2 to 50. These grains are described in U.S. Patent 5,264,337, 5,314,798 and 5,320,958 and desired tabular grains can be readily obtained. Silver halide grains having rounded corners are also preferably employed.

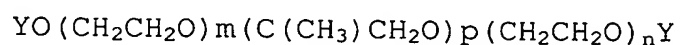
Crystal habit of the outer surface of the silver halide grains is not specifically limited, but in cases when using a spectral sensitizing dye exhibiting crystal habit (face) selectivity in the adsorption reaction of the sensitizing dye onto the silver halide grain surface, it is preferred to use silver halide grains having a relatively high proportion of the crystal habit meeting the selectivity. In cases when using a sensitizing dye selectively adsorbing onto the crystal face of a Miller index of [100], for example, a high ratio accounted for by a Miller index [100] face is preferred. This ratio is preferably at least 50%; is more preferably at least 70%, and is most preferably at least 80%. The ratio accounted for by the Miller index [100] face can be

obtained based on T. Tani, J. Imaging Sci., 29, 165 (1985) in which adsorption dependency of a [111] face or a [100] face is utilized.

It is preferred to use low molecular gelatin having an average molecular weight of not more than 50,000 in the preparation of silver halide grains used in the invention, specifically, in the stage of nucleation. Thus, the low molecular gelatin has an average molecular weight of not more than 50,000, preferably 2,000 to 40,000, and more preferably 5,000 to 25,000. The average molecular weight can be determined by means of gel permeation chromatography. The low molecular weight gelatin can be obtained by subjecting an aqueous gelatin conventionally used and having an average molecular weight of ca. 100,000 to enzymatic hydrolysis, acid or alkali hydrolysis, thermal degradation at atmospheric pressure or under high pressure, or ultrasonic degradation.

The concentration of dispersion medium used in the nucleation stage is preferably not more than 5% by weight, and more preferably 0.05 to 3.0% by weight.

In the preparation of silver halide grains, it is preferred to use a compound represented by the following formula, specifically in the nucleation stage:



where Y is a hydrogen atom,  $-\text{SO}_3\text{M}$  or  $-\text{CO}-\text{B}-\text{COOM}$ , in which M is a hydrogen atom, alkali metal atom, ammonium group or ammonium group substituted by an alkyl group having carbon atoms of not more than 5, and B is a chained or cyclic group forming an organic dibasic acid; m and n each are 0 to 50; and p is 1 to 100. Polyethylene oxide compounds represented by foregoing formula have been employed as a defoaming agent to inhibit marked foaming occurred when stirring or moving emulsion raw materials, specifically in the stage of preparing an aqueous gelatin solution, adding a water-soluble silver and halide salts to the aqueous gelatin solution or coating an emulsion on a support during the process of preparing silver halide photographic light sensitive materials. A technique of using these compounds as a defoaming agent is described in JP-A No. 44-9497. The polyethylene oxide compound represented by the foregoing formula also functions as a defoaming agent during nucleation. The compound represented by the foregoing formula is used preferably in an amount of not more than 1%, and more preferably 0.01 to 0.1% by weight, based on silver.

The compound is to be present at the stage of nucleation, and may be added to a dispersing medium prior to or during nucleation. Alternatively, the compound may be

added to an aqueous silver salt solution or halide solution used for nucleation. It is preferred to add it to a halide solution or both silver salt and halide solutions in an amount of 0.01 to 2.0% by weight. It is also preferred to make the compound represented by formula [5] present over a period of at least 50% (more preferably, at least 70%) of the nucleation stage.

The temperature during the stage of nucleation is preferably 5 to 60° C, and more preferably 15 to 50° C. Even when nucleation is conducted at a constant temperature, in a temperature-increasing pattern (e.g., in such a manner that nucleation starts at 25° C and the temperature is gradually increased to reach 40° C at the time of completion of nucleation) or its reverse pattern, it is preferred to control the temperature within the range described above.

Silver salt and halide salt solutions used for nucleation are preferably in a concentration of not more than 3.5 mol/l, and more preferably 0.01 to 2.5 mol/l. The flow rate of aqueous silver salt solution is preferably  $1.5 \times 10^{-3}$  to  $3.0 \times 10^{-1}$  mol/min per liter of the solution, and more preferably  $3.0 \times 10^{-3}$  to  $8.0 \times 10^{-2}$  mol/min. per liter of the solution. The pH during nucleation is within a range of 1.7 to 10, and since the pH at the alkaline side broadens the



grain size distribution, the pH is preferably 2 to 6. The pBr during nucleation is 0.05 to 3.0, preferably 1.0 to 2.5, and more preferably 1.5 to 2.0.

Silver halide may be incorporated into an image forming layer by any means, in which silver halide is arranged so as to be as close to reducible silver source (aliphatic carboxylic acid silver salt) as possible. It is general that silver halide, which has been prepared in advance, added to a solution used for preparing an organic silver salt. In this case, preparation of silver halide and that of an organic silver salt are separately performed, making it easier to control the preparation thereof. Alternatively, as described in British Patent 1,447,454, silver halide and an organic silver salt can be simultaneously formed by allowing a halide component to be present together with an organic silver salt-forming component and by introducing silver ions thereto. Silver halide can also be prepared by reacting a halogen containing compound with an organic silver salt through conversion of the organic silver salt. Thus, a silver halide-forming component is allowed to act onto a pre-formed organic silver salt solution or dispersion or a sheet material containing an organic silver salt to convert a part of the organic silver salt to photosensitive silver halide.

The silver halide-forming components include inorganic halide compounds, onium halides, halogenated hydrocarbons, N-halogeno compounds and other halogen containing compounds. These compounds are detailed in U.S. Patent 4,009,039, 3,457,075 and 4,003,749, British Patent 1,498,956 and JP-A 53-27027 and 53-25420. Exemplary examples thereof include inorganic halide compound such as a metal halide and ammonium halide; onium halides, such as trimethylphenylammonium bromide, cetyldimethylammonium bromide, and trimethylbenzylammonium bromide; halogenated hydrocarbons, such as iodoform, bromoform, carbon tetrachloride and 2-bromo-2-methylpropane; N-halogenated compounds, such as N-bromosuccinimide, N-bromophthalimide, and N-bromoacetamide; and other halogen containing compounds, such as triphenylmethyl chloride, triphenylmethyl bromide, 2-bromoacetic acid, 2-bromoethanol and dichlorobenzophenone. As described above, silver halide can be formed by converting a part or all of an organic silver salt to silver halide through reaction of the organic silver salt and a halide ion. The silver halide separately prepared may be used in combination with silver halide prepared by conversion of at least a part of an organic silver salt. The silver halide which is separately prepared or prepared through conversion

of an organic silver salt is used preferably in an amount of 0.001 to 0.7 mol, and more preferably 0.03 to 0.5 mol per mol of organic silver salt.

Silver halide used in the invention preferably occludes ions of metals belonging to Groups 6 to 11 of the Periodic Table. Preferred as the metals are W; Fe, Co, Ni, Cu, Ru, Rh, Pd, Re, Os, Ir, Pt and Au. These metals may be introduced into silver halide in the form of a complex. The content thereof is preferably  $1 \times 10^{-9}$  to  $1 \times 10^{-2}$ , and more preferably  $1 \times 10^{-8}$  to  $1 \times 10^{-4}$  mol per mol of silver. In this invention, a transition metal complex or its complex ion represented by the following formula (5) described below is preferred:

formula (5):  $(ML_6)^m$ :

wherein M represents a transition metal selected from elements in Groups 6 to 11 of the Periodic Table; L represents a coordinating ligand; and m represents 0, 1-, 2-, 3- or 4-. Exemplary examples of the ligand represented by L include halides (fluoride, chloride, bromide, and iodide), cyanide, cyanato, thiocyanato, selenocyanato, tellurocyanato, azido and aquo, nitrosyl, thionitrosyl, etc., of which aquo, nitrosyl and thionitrosyl are preferred. When the aquo

ligand is present, one or two ligands are preferably coordinated. L may be the same or different.

Compounds, which provide these metal ions or complex ions, are preferably incorporated into silver halide grains through addition during the silver halide grain formation. These may be added during any preparation stage of the silver halide grains, that is, before or after nuclei formation, growth, physical ripening, and chemical ripening. However, these are preferably added at the stage of nuclei formation, growth, and physical ripening; furthermore, are preferably added at the stage of nuclei formation and growth; and are most preferably added at the stage of nuclei formation. These compounds may be added several times by dividing the added amount. Uniform content in the interior of a silver halide grain can be carried out. As disclosed in JP-A No. 63-29603, 2-306236, 3-167545, 4-76534, 6-110146, 5-273683, the metal can be non-uniformly occluded in the interior of the grain.

These metal compounds can be dissolved in water or a suitable organic solvent (e.g., alcohols, ethers, glycols, ketones, esters, amides, etc.) and then added. Furthermore, there are methods in which, for example, an aqueous metal compound powder solution or an aqueous solution in which a

metal compound is dissolved along with NaCl and KCl is added to a water-soluble silver salt solution during grain formation or to a water-soluble halide solution; when a silver salt solution and a halide solution are simultaneously added, a metal compound is added as a third solution to form silver halide grains, while simultaneously mixing three solutions; during grain formation, an aqueous solution comprising the necessary amount of a metal compound is placed in a reaction vessel; or during silver halide preparation, dissolution is carried out by the addition of other silver halide grains previously doped with metal ions or complex ions. Specifically, the preferred method is one in which an aqueous metal compound powder solution or an aqueous solution in which a metal compound is dissolved along with NaCl and KCl is added to a water-soluble halide solution. When the addition is carried out onto grain surfaces, an aqueous solution comprising the necessary amount of a metal compound can be placed in a reaction vessel immediately after grain formation, or during physical ripening or at the completion thereof or during chemical ripening.

Silver halide grain emulsions used in the invention may be desalted after the grain formation, using the methods

known in the art, such as the noodle washing method and flocculation process.

Light-insensitive organic silver salts used in the invention are reducible silver source, and silver salts of organic acids are preferred and organic acids usable in this invention include an aliphatic carboxylic acids, carbocyclic carboxylic acids, heterocyclic carboxylic acids and heterocyclic compounds.

The organic silver salts used in the invention are described in Research Disclosure (hereinafter, also denoted simply as RD) 17029 and 29963, including silver salts of aliphatic carboxylic acids (e.g., gallic acid, oxalic acid, behenic acid, stearic acid, palmitic acid, lauric acid, etc.); carboxyalkylthiourea silver salts (e.g., 1-(3-carboxypropyl)thiourea, 1-(3-carboxypropyl)-3,3-dimethylthiourea, etc.); silver complexes of polymer reaction products of aldehyde with hydroxy-substituted aromatic carboxylic acid (e.g., aldehydes such as formaldehyde, acetaldehyde, butylaldehyde), hydroxy-substituted acids (e.g., salicylic acid, benzoic acid, 3,5-dihydroxybenzoic acid, 5,5-thiodisalicylic acid, silver salts or complexes of thiones (e.g., 3-(2-carboxyethyl)-4-hydroxymethyl-4-(thiazoline-2-thione and 3-carboxymethyl-4-thiazoline-2-

thione), complexes of silver with nitrogen acid selected from imidazole, pyrazole, urazole, 1,2,4-thiazole, and 1H-tetrazole, 3-amino-5-benzylthio-1,2,4-triazole and benztriazole or salts thereof; silver salts of saccharin, 5-chlorosalicylaldoxime, etc.; and silver salts of mercaptides. Of these organic silver salts, silver salts of aliphatic carboxylic acids having 10 to 30 carbon atoms (more preferably 15 to 25 carbon atoms) are preferred, and silver salts of gallic acid, oxalic acid, behenic acid, arachidic acid and/or stearic acid are specifically preferred. A mixture of two or more kinds of organic silver salts is preferably used, enhancing developability and forming silver images exhibiting relatively high density and high contrast. For example, preparation by adding a silver ion solution to a mixture of two or more kinds of organic acids is preferable.

The aliphatic carboxylic acid silver salt compound can be obtained by mixing an aqueous-soluble silver compound with a compound capable of forming a complex. Normal precipitation, reverse precipitation, double jet precipitation and controlled double jet precipitation, as described in JP-A 9-127643 are preferably employed. For example, to an organic acid can be added an alkali metal hydroxide (e.g., sodium hydroxide, potassium hydroxide, etc.)

to form an alkali metal salt soap of the organic acid (e.g., sodium behenate, sodium arachidate, etc.), thereafter, the soap and silver nitrate are mixed by the controlled double jet method to form organic silver salt crystals. In this case, silver halide grains may be concurrently present.

The silver salt grains used in this invention preferably have an average circular equivalent diameter of 0.05 to 0.8  $\mu\text{m}$  (more preferably 0.2 to 0.5  $\mu\text{m}$ ) in terms of enhancement of transparency and storage stability of developed silver images and preferably an average grain thickness of 0.005 to 0.07  $\mu\text{m}$  (more preferably, 0.01 to 0.05  $\mu\text{m}$ ) in terms of optimum silver ion supply and storage stability of silver images.

The grain diameter was determined in the following manner. An organic silver salt dispersion was diluted, dispersed on the grid provided with a carbon support membrane, and then photographed at a direct magnification of 5,000 times using a transmission type electron microscope (TEM, 2000 FX type, available from Nihon Denshi Co., Ltd.). The thus obtained negative electron micrographic images were read as a digital image by a scanner to determine the diameter (circular equivalent diameter) using appropriate



software. At least 300 grains were so measured to determine an average diameter.

The grain thickness is determined using a transmission type electron microscope in the following manner. First, a light sensitive layer, coated onto a support, is pasted onto a suitable holder employing an adhesive and is cut perpendicular to the support surface employing a diamond knife to prepare an ultra-thin slice, at a thickness of 0.1 to 0.2  $\mu\text{m}$ . The thus prepared ultra-thin slice is supported on a copper mesh, and is placed onto a carbon membrane, which has been made to be hydrophilic by means of a glow discharge. Then, while cooling the resulting slice to not more than  $-130^{\circ}\text{C}$ , the image in a bright visual field is observed at a magnification of 5,000 to 40,000 employing a transmission electron microscope (hereinafter referred to as TEM), and then images are quickly recorded employing an image plate, a CCD camera, etc. In such a case, it is recommended to suitably select a portion of said slice, which has neither been torn nor distorted in the visual field for observation.

The carbon membrane, which is supported by an organic film such as an extremely thin collodion, Formvar, etc., is preferably employed, and a film composed of only carbon, which is obtained by forming the film on a rock salt

substrate and then dissolving away the substrate or by removing the foregoing organic film, employing an organic solvent or ion etching, is more preferably employed. The acceleration voltage of said TEM is preferably 80 to 400 kV, and is most preferably 80 to 200 kV.

Details of other means such as electron microscopic technology and sample preparation techniques can be referred to in "Igaku·Seibutsugaku Denshikenbikyo Kansatsuho (Medical and Biological Electron Microscopy", edited by Nippon Denshikenbikyo Gakkai, Kanto-Shibu, (Maruzen), and "Denshikenbikyo Seibutsu Shiryo Sakuseiho (Preparation Method of Biological Samples for Electron Microscopy)", edited by Nippon Denshikenbikyo Gakkai, Kanto-Shibu, (Maruzen).

The TEM image, recorded in an appropriate medium, is decomposed to at least  $1024 \times 1024$  pixels or preferably at least  $2048 \times 2048$  pixels, and is then subjected to image processing employing a computer. In order to carry out image processing, an analogue image recorded on a film strip is converted into a digital image employing a scanner etc., and the resulting image is preferably subjected to shading correction, contrast-edge enhancement, etc., based on

specific requirements. Thereafter, a histogram is prepared and the portions corresponding to organic silver are extracted employing binary processing. At least 300 grains of the organic silver salt were manually measured with respect to the thus extracted thickness employing appropriate software.

Methods to prepare organic silver salt grains having the above-mentioned shape are not particularly restricted. The optimization of various conditions such as maintaining the mixing state during the formation of an organic acid alkali metal salt soap and/or the mixing state during the addition of silver nitrate to said soap. After tabular organic silver salt grains employed in the present invention are preliminarily dispersed together with binders, surface active agents, etc., if desired, the resulting mixture is preferably dispersed and pulverized by a media homogenizer, a high pressure homogenizer, or the like. During said preliminary dispersion, ordinary stirrers such as an anchor type, a propeller type, etc., a high-speed rotation centrifugal radial type stirrer (Dissolver), as a high speed shearing stirrer (homomixer) may be employed.

Furthermore, employed as said media homogenizers may be rolling mills such as a ball mill, a satellite ball mill, a

vibrating ball mill, medium agitation mills such as a bead mill, attriter, and others such as a basket mill. Employed as high pressure homogenizers may be various types such as a type in which collision occurs against a wall or a plug, a type in which liquid is divided into a plurality of portions and said portions are subjected to collision with each other, a type in which liquid is forced to pass through a narrow orifice, etc. Examples of ceramics employed as the ceramic beads include  $\text{Al}_2\text{O}_3$ ,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{MgO}$ ,  $\text{ZrO}$ ,  $\text{BeO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_3$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3\text{-MgO}$ ,  $\text{MgO-CaO}$ ,  $\text{MoO-C}$ ,  $\text{MgO-Al}_2\text{O}_3$  (spinel),  $\text{SiC}$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{BaO}$ ,  $\text{PbO}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{BeAl}_2\text{O}_4$ ,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  (cubic zirconia),  $3\text{BeO-Al}_2\text{O}_3\text{-6SiO}_2$  (artificial emerald),  $\text{C}$  (artificial diamond),  $\text{SiO}_2\text{-nH}_2\text{O}$ , silicone nitride, yttrium-stabilized-zirconia, zirconia-reinforced-alumina. Yttrium-stabilized-zirconia and zirconia-reinforced-alumina are preferably employed in view that little impurity is generated by friction among the beads or the classifier during classifying them. The ceramics containing zirconia are called zirconia as an abbreviation.

In devices employed for dispersing the tabular organic silver salt grains employed in the present invention, preferably employed as the members which are in contact with the organic silver salt grains are ceramics such as zirconia,

alumina, silicone nitride, boron nitride, or diamond. Of these, zirconia is the one most preferably employed. While carrying out of the above-mentioned dispersion, the binder is preferably added so as to achieve a concentration of 0.1 to 10 wt% with reference to the weight of the organic silver salt, and the temperature is preferably maintained at no less than 45° C from the preliminary dispersion to the main dispersion process. An example of the preferable operation conditions of a homogenizer, when employing high-pressure homogenizer as the dispersing machine, is twice or more operations at 300 to 1,000 kgf/cm<sup>2</sup>. In the case when a media-dispersing machine is employed, a circumferential speed of 6 to 13 m/sec. is preferable.

In the preparation process of organic silver salt grains, it is preferred to prepare aliphatic carboxylic acid silver salt grains concurrently in the presence of a compound capable of functioning as a crystal growth retarding agent or dispersing agent for aliphatic carboxylic acid silver salt grains. The compound capable of functioning as a crystal growth retarding agent or dispersing agent for aliphatic carboxylic acid silver salt grains refers to one which has a function or effect of forming grains with reduced size and enhanced uniformity thereof when prepared in the presence of

the compound, as compared to the absence thereof. Specific examples of such compounds include monohydric alcohols having 10 or less carbon atoms (preferably secondary and tertiary alcohols), glycols such as ethylene glycol and propylene glycol, poly-ethers such as polyethylene glycol, and glycerin. Such compounds are added in an amount of 10 to 200% by weight, based on aliphatic carboxylic acid silver salt.

Branched aliphatic carboxylic acids including isomers thereof are also preferable, such as iso-heptanoic acid, iso-decanoic acid, iso-tridecanoic acid, iso-myristic acid, iso-palmitic acid, iso-stearic acid, iso-arachidic acid, iso-behenic acid and iso-hexanoic acid. In this case, a preferable branched chain is an alkyl or alkenyl group having 4 or less carbon atoms. Further, unsaturated aliphatic carboxylic acids are cited, such as palmithreic acid, oleic acid, linolic acid, linoleic acid, moroctic acid, eicosenic acid, arachidonic acid, eicopentaenic acid, erucic acid, docosapentaenic acid, and selacholeic acid. These compounds are added in an amount of 0.5 to 10 mol%, based on aliphatic carboxylic acid silver salt.

Preferred compounds include glycosides such as gluciside, galactoside and fructoside; trehalose type

disaccharides such as trahalose and sucrose; polysaccharides such as glycogen, dextrin, dextran and alginic acidcellosolves such as methyl cellosolve and ethyl cellosolve; water-soluble organic solvents such as sorbitan, sorbitol, ethyl acetate, methyl acetate, and dimethyl formamide; water-soluble polymers such as polyvinyl alcohol, polyacrylic acid, acrylic acid copolymer, maleic acid copolymer, carboxymethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, polyvinyl pyrrolidone and gelatin. These compounds are added preferably in an amount of 0.1 to 20% by weight.

Alcohols having 10 or less carbon atoms are preferred, and the use of secondary or tertiary alcohols enhances solubility of sodium salt of an aliphatic carboxylic acid, resulting in reduced viscosity and enhancing stirring efficiency, leading to formation of monodisperse fine grains. Branched aliphatic carboxylic acids and unsaturated carboxylic acids exhibit higher steric hindrance than straight chain aliphatic carboxylic acids, resulting in fine crystals due to increased disorder in crystal lattice.

With regard to the difference in constitution between a conventional silver salt photographic material and a photothermographic imaging material, the photothermographic

imaging material contains relatively large amounts of light sensitive silver halide, a carboxylic acid silver salt and a reducing agent which often cause fogging and silver printing-out (print out silver). In the photothermographic imaging material, therefore, an enhanced technique for antifogging and image-lasting is needed to maintain storage stability not only before development but also after development. In addition to commonly known aromatic heterocyclic compounds to restrain growth of fog specks and development thereof, there were used mercury compounds having a function of allowing the fog specks to oxidatively die away. However, such a mercury compound causes problems with respect to working safety and environment protection.

Next, antifoggants and image stabilizers used in the photothermographic imaging material relating to the invention will be described.

In photothermographic materials relating to this invention are employed reducing agents containing a proton, such as bisphenols and sulfonamidophenols. Accordingly, a compound generating a labile species which is capable of abstracting a proton to deactivate the reducing agent is preferred. More preferred is a compound as a non-colored photo-oxidizing substance, which is capable of generating a

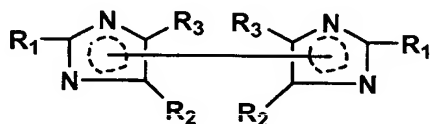


free radical as a labile species on exposure. Any compound having such a function is applicable. However, a halogen radical, which easily forms silver halide is not preferred. An organic free radical composed of plural atoms is preferred. Any compound having such a function and exhibiting no adverse effect on the photothermographic material is usable irrespective of its structure.

Of such free radical generation compounds, a compound containing an aromatic, and carbocyclic or heterocyclic group is preferred, which provides stability to the generated free radical so as to be in contact with the reducing agent for a period sufficient to react with the reducing agent to deactivate it. Representative examples of such compounds include biimidazolyl compounds and iodonium compounds.

Of such imidazolyl compounds, a compound represented by the following formula [1] is preferred:

formula [1]



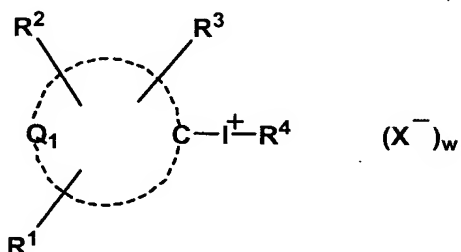
wherein  $R_1$ ,  $R_2$  and  $R_3$ , which may be the same or different, are each a hydrogen atom, an alkyl group, an alkenyl group, an alkoxy group, an aryl group, hydroxy, a halogen atom, an

aryloxyl, an alkylthio group, an arylthio group, an acyl group a sulfonyl group, an acylamino group, sulfonylamino group, an acyloxy group, carboxy, cyano, a sulfo group, or an amino group. Of these groups are preferred an aryl group, an alkenyl group and cyano group.

The biimidazolyl compounds can be synthesized in accordance with the methods described in U.S. Patent 3,734,733 and British Patent 1,271,177. Preferred Examples thereof are described in JP-A 2000-321177.

Similarly preferred compounds include an iodonium compound represented by the following formula [2]:

formula [2]

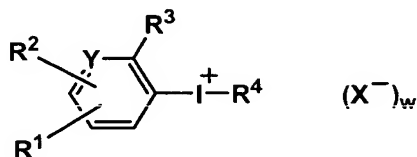


wherein Q<sub>1</sub> is a group of atoms necessary to complete a 5-, 6-, or 7-membered ring, and the atoms being selected from a carbon atom, nitrogen atom, oxygen atom and sulfur atom; and R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> (,which may be the same or different) are each a hydrogen atom, an alkyl group (e.g., methyl, ethyl, hexyl), an alkenyl group (e.g., vinyl, allyl), an alkoxy group (e.g., methoxy, ethoxy, octyloxy), an aryl group (e.g.,

phenyl, naphthyl, tolyl), hydroxy, a halogen atom, an aryloxy (e.g., phenoxy), an alkylthio group (e.g., methylthio, butylthio), an arylthio group (e.g., phenylthio), an acyl group (e.g., acetyl, propionyl, butyryl, valeryl), a sulfonyl group (e.g., methylsulfonyl, phenylsulfonyl), an acylamino group, sulfonylamino group, an acyloxy group (e.g., acetoxy, benzoxy), carboxy, cyano, a sulfo group, or an amino group. Of these groups are preferred an aryl group, an alkenyl group and cyano group, provided that  $R^1$ ,  $R^2$  and  $R^3$  may be bonded with each other to form a ring;  $R^4$  is a carboxylate group such as acetate, benzoate or trifluoroacetate, or  $O^-$ ;  $W$  is 0 or 1, provided that when  $R^3$  is a sulfo group or a carboxy group,  $W$  is 0, and  $R^4$  is  $O^-$ ;  $X^-$  is an anionic counter ion, and preferably  $CH_3CO_2^-$ ,  $CH_3SO_3^-$  or  $PF_6^-$ .

Of these is specifically preferred a compound represented by the following formula [3]:

formula [3]



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $X^-$  and  $W$  are each the same as defined in formula [2];  $Y$  is a carbon (i.e.,  $-CH=$ ) to form a benzene ring or a nitrogen atom ( $-N=$ ) to form a pyridine ring.

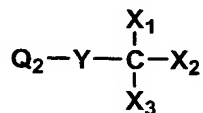
The iodonium compounds described above can be synthesized in accordance with the methods described in Org. Syn., 1961 and Fieser, "Advanced Organic Chemistry" (Reinhold, N.Y., 1961). Specific examples thereof are include those described in JP-A 2000-321711.

The compounds represented by the foregoing formula [1], [2] or [3] are incorporated at  $10^{-3}$  to  $10^{-1}$  mol, and preferably  $5 \times 10^{-3}$  to  $5 \times 10^{-2}$  mol/m<sup>2</sup>. The compounds may be incorporated into any of constituting layers of the photothermographic material and preferably in the vicinity of a reducing agent.

As a compound capable of deactivating a reducing agent to inhibit reduction of an organic silver salt to silver by the reducing agent are preferred compounds releasing a labile species other than a halogen atom. However, these compounds may be used in combination with a compound capable of releasing a halogen atom as a labile species.

Examples of the compound releasing an active halogen atom include a compound represented by the following formula [4]:

formula [4]



wherein  $Q_2$  is an aryl group or a heterocyclic group;  $X_1$ ,  $X_2$  and  $X_3$  are each a hydrogen atom, a halogen atom, a haloalkyl group, an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a sulfonyl group, an aryl group or a heterocyclic group, provided that at least of them a halogen atom;  $Y$  is  $-C(=O)-$ ,  $-SO-$  or  $-SO_2-$ . The aryl group represented by  $Q_2$  may be a monocyclic group or condensed ring group and is preferably a monocyclic or di-cyclic aryl group having 6 to 30 carbon atoms (e.g., phenyl, naphthyl), more preferably a phenyl or naphthyl group, and still more preferably a phenyl group. The heterocyclic group represented by  $Q_2$  is a 3- to 10-membered, saturated or unsaturated heterocyclic group containing at least one of N, O and S, which may be a monocyclic or condensed with another ring to a condensed ring. Substituents are detailed in JP-A No. 2001-263350, paragraph [0100] through [0103].

The heterocyclic group is preferably a 5- or 6-membered unsaturated heterocyclic group, which may be condensed, more preferably a 5- or 6-membered aromatic heterocyclic group, which may be condensed, still more preferably a N-containing 5- or 6-membered aromatic heterocyclic group, which may be condensed, and optimally a 5- or 6-membered aromatic heterocyclic group containing one to four N atoms, which may

be condensed. Exemplary examples of heterocyclic rings included in the heterocyclic group include imidazole, pyrazole, pyridine, pyrimidine, pyrazine, pyridazine, triazole, triazines, indole, indazole, purine, thiazole, oxadiazole, quinoline, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, pteridine, acrydine, phenanthroline, phenazine, tetrazole, thiazole, oxazole, benzimidazole, benzoxazole, benzthiazole, indolenine and tetrazaindene. Of these are preferred imidazole, pyridine, pyrimidine, pyrazine, pyridazine, triazole, triazines, thiadiazole, oxadiazole, quinoline, phthalazine, naphthylizine, quinoxaline, quinazoline, cinnoline, tetrazole, thiazole, oxazole, benzimidazole, and tetrazaindene; more preferably imidazole, pyrimidine, pyridine, pyrazine, pyridazine, triazole, triazines, thiadiazole, quinoline, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, tetrazole, thiazole, benzimidazole, and benzthiazole; and still more preferably pyridine, thiazole, quinoline and benzthiazole.

The aryl group or heterocyclic group represented by Q may be substituted by a substituent, in addition to  $-Y-C(X_1)(X_2)(X_3)$ . Preferred examples of the substituent include an alkyl group, an alkenyl group, an aryl group, an

alkoxyl group, an aryloxyl group, an acyloxy group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, an acylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonylamino group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, a ureido group, phosphoramido group, a halogen atom, cyano group, sulfo group, carboxy group, nitro group and heterocyclic group. Of these are preferred an alkyl group, an aryl group, an alkoxyl group, an aryloxyl group, an acyl group, an acylamino group, an aryloxyl group, acyl group, an acylamino group, an alkoxycarbonyl group, an aryloxycarbonylamino group, a sulfonylamino group, a sulfamoyl group, a carbamoyl group, a ureido group, phosphoramido group, a halogen atom, cyano group, nitro group, and a heterocyclic group; and more preferably an alkyl group, an aryl group, an alkoxyl group, an aryloxyl group, an acyl group, an acylamino group, a sulfonylamino group, a sulfamoyl group, a carbamoyl group, a halogen group, cyano group, nitro group and a heterocyclic group; and still more preferably an alkyl group, an aryl group and a halogen atom.  $X_1$ ,  $X_2$  and  $X_3$  are preferably a halogen atom, a haloalkyl group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a sulfamoyl group,

a sulfonyl group, and a heterocyclic group, more preferably a halogen atom, a haloalkyl group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, and a sulfonyl group; and still more preferably a halogen atom and trihalomethyl group; and most preferably a halogen atom. Of halogen atoms are preferably chlorine atom, bromine and iodine atom, and more preferably chlorine atom and bromine atom, and still more preferably bromine atom. Y is  $-C(=O)-$ ,  $-SO-$ , and  $-SO_2-$ , and preferably  $-SO_2-$ .

The amount of this compound to be incorporated is preferably within the range in which an increase of printed-out silver caused by formation of silver halide becomes substantially no problem, more preferably not more than 150% by weight and still more preferably not more than 100% by weight, based on the compound releasing no active halogen atom.

Further, in addition to the foregoing compounds, compounds commonly known as an antifoggant may be incorporated in the photothermographic imaging material used in the invention. In such a case, the compounds may be those which form a labile species similarly to the foregoing compounds or those which are different in antifogging mechanism. Examples thereof include compounds described in



U.S. Patent Nos. 3,589,903, 4,546,075 and 4,452,885; JP-A No. 59-57234; U.S. Patent Nos. 3,874,946 and 4,756,999; and JP-A Nos. 9-288328 and 9-90550. Further, other antifoggants include, for example, compounds described in U.S. Patent No. 5,028,523 and European patent Nos. 600,587, 605,981 and 631,176.

Silver halide grains used in the invention can be subjected to chemical sensitization. In accordance with methods described in Japanese Patent Application Nos. 2000-57004 and 2000-61942, for example, a chemical sensitization center (chemical sensitization speck) can be formed using compounds capable of releasing chalcogen such as sulfur or noble metal compounds capable of releasing a noble metal ion such as a gold ion. In the invention, it is preferred to conduct chemical sensitization with an organic sensitizer containing a chalcogen atom, as described below. Such a chalcogen atom-containing organic sensitizer is preferably a compound containing a group capable of being adsorbed onto silver halide and a labile chalcogen atom site. These organic sensitizers include, for example, those having various structures, as described in JP-A Nos. 60-150046, 4-109240 and 11-218874. Specifically preferred of these is at least a compound having a structure in which a chalcogen atom

is attacked to a carbon or phosphorus atom through a double bond. The amount of a chalcogen compound added as an organic sensitizer is variable, depending on the chalcogen compound to be used, silver halide grains and a reaction environment when subjected to chemical sensitization and is preferably  $10^{-8}$  to  $10^{-2}$  mol, and more preferably  $10^{-7}$  to  $10^{-3}$  mol per mol of silver halide. In the invention, the chemical sensitization environment is not specifically limited but it is preferred to conduct chemical sensitization in the presence of a compound capable of eliminating a silver chalcogenide or silver specks formed on the silver halide grain or reducing the size thereof, or specifically in the presence of an oxidizing agent capable of oxidizing the silver specks, using a chalcogen atom-containing organic sensitizer. To conduct chemical sensitization under preferred conditions, the pAg is preferably 6 to 11, and more preferably 7 to 10, the pH is preferably 4 to 10 and more preferably 5 to 8, and the temperature is preferably not more than 30° C.

In photothermographic imaging materials used in the invention, it is preferred to use a light sensitive emulsion, in which light sensitive silver halide has been subjected to chemical sensitization using a chalcogen atom-containing

organic sensitizer at a temperature of 30° C or higher, concurrently in the presence of an oxidizing agent capable of oxidizing silver specks formed on the silver halide grains, then, mixed with an organic silver salt, dehydrated and dried.

Chemical sensitization using the foregoing organic sensitizer is also preferably conducted in the presence of a spectral sensitizing dye or a heteroatom-containing compound capable of being adsorbed onto silver halide grains. Thus, chemical sensitization in the presence of such a silver halide-adsorptive compound results in prevention of dispersion of chemical sensitization center specks, thereby achieving enhanced sensitivity and minimized fogging. Although there will be described spectral sensitizing dyes used in the invention, preferred examples of the silver halide-adsorptive, heteroatom-containing compound include nitrogen containing heterocyclic compounds described in JP-A No. 3-24537. In the heteroatom-containing compound, examples of the heterocyclic ring include a pyrazolo ring, pyrimidine ring, 1,2,4-triazole ring, 1,2,3-triazole ring, 1,3,4-thiazole ring, 1,2,3-thiadiazole ring, 1, 2, 4-thiadiazole ring, 1,2,5-thiadiazole ring, 1,2,3,4-tetrazole ring, pyridazine ring, 1,2,3-triazine ring, and a condensed ring of

two or three of these rings, such as triazolotriazole ring, diazaindene ring, triazaindene ring and pentazaindene ring. Condensed heterocyclic ring comprised of a monocyclic hetero-ring and an aromatic ring include, for example, a phthalazine ring, benzimidazole ring indazole ring, and benzthiazole ring. Of these, an azaindene ring is preferred and hydroxy-substituted azaindene compounds, such as hydroxytriazaindene, tetrahydroxyazaindene and hydroxypentazaundene compound are more preferred. The heterocyclic ring may be substituted by substituent groups other than hydroxy group. Examples of the substituent group include an alkyl group, substituted alkyl group, alkylthio group, amino group, hydroxyamino group, alkylamino group, dialkylamino group, arylamino group, carboxy group, alkoxycarbonyl group, halogen atom and cyano group. The amount of the heterocyclic ring containing compound to be added, which is broadly variable with the size or composition of silver halide grains, is within the range of  $10^{-6}$  to 1 mol, and preferably  $10^{-4}$  to  $10^{-1}$  mol per mol silver halide.

As described earlier, silver halide grains can be subjected to noble metal sensitization using compounds capable of releasing noble metal ions such as a gold ion. Examples of usable gold sensitizers include chloroaurates and

organic gold compounds. In addition to the foregoing sensitization, reduction sensitization can also be employed and exemplary compounds for reduction sensitization include ascorbic acid, thiourea dioxide, stannous chloride, hydrazine derivatives, borane compounds, silane compounds and polyamine compounds. Reduction sensitization can also be conducted by ripening the emulsion while maintaining the pH at not less than 7 or the pAg at not more than 8.3. Silver halide to be subjected to chemical sensitization may be one which has been prepared in the presence of an organic silver salt, one which has been formed under the condition in the absence of the organic silver salt, or a mixture thereof.

Light sensitive silver halide grains used in the invention are preferably subjected to spectral sensitization by allowing a spectral sensitizing dye to adsorb to the grains. Examples of the spectral sensitizing dye include cyanine, merocyanine, complex cyanine, complex merocyanine, holo-polar cyanine, styryl, hemicyanine, oxonol and hemioxonol dyes, as described in JP-A Nos. 63-159841, 60-140335, 63-231437, 63-259651, 63-304242, 63-15245; U.S. Patent Nos. 4,639,414, 4,740,455, 4,741,966, 4,751,175 and 4,835,096. Usable sensitizing dyes are also described in Research Disclosure (hereinafter, also denoted as RD) 17643,

page 23, sect. IV-A (December, 1978), and *ibid* 18431, page 437, sect. X (August, 1978). It is preferred to use sensitizing dyes exhibiting spectral sensitivity suitable for spectral characteristics of light sources of various laser imagers or scanners. Examples thereof include compounds described in JP-A Nos. 9-34078, 9-54409 and 9-80679.

Useful cyanine dyes include, for example, cyanine dyes containing a basic nucleus, such as thiazoline, oxazoline, pyrroline, pyridine, oxazole, thiazole, selenazole and imidazole nuclei. Useful merocyanine dyes preferably contain, in addition to the foregoing nucleus, an acidic nucleus such as thiohydantoin, rhodanine, oxazolidine-dione, thiazoline-dione, barbituric acid, thiazolinone, malononitrile and pyrazolone nuclei. In the invention, there are also preferably used sensitizing dyes having spectral sensitivity within the infrared region. Examples of the preferred infrared sensitizing dye include those described in U.S. Patent Nos. 4,536,478, 4,515,888 and 4,959,294.

The infrared sensitizing dye relating to the invention is preferably a long chain polymethine dye, in which a sulfinyl group is substituted on the benzene ring of the benzothiazole ring.

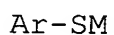
The infrared sensitizing dyes and spectral sensitizing dyes described above can be readily synthesized according to the methods described in F.M. Hammer, The Chemistry of Heterocyclic Compounds vol.18, "The cyanine Dyes and Related Compounds" (A. Weissberger ed. Interscience Corp., New York, 1964).

The infrared sensitizing dyes can be added at any time after preparation of silver halide. For example, the dye can be added to a light sensitive emulsion containing silver halide grains/organic silver salt grains in the form of by dissolution in a solvent or in the form of a fine particle dispersion, so-called solid particle dispersion. Similarly to the heteroatom containing compound having adsorptivity to silver halide, after adding the dye prior to chemical sensitization and allowing it to be adsorbed onto silver halide grains, chemical sensitization is conducted, thereby preventing dispersion of chemical sensitization center specks and achieving enhanced sensitivity and minimized fogging.

These sensitizing dyes may be used alone or in combination thereof. The combined use of sensitizing dyes is often employed for the purpose of supersensitization. A super-sensitizing compound, such as a dye which does not exhibit spectral sensitization or substance which does not

substantially absorb visible light may be incorporated, in combination with a sensitizing dye, into the emulsion containing silver halide grains and organic silver salt grains used in photothermographic imaging materials of the invention.

Useful sensitizing dyes, dye combinations exhibiting super-sensitization and materials exhibiting supersensitization are described in RD17643 (published in December, 1978), IV-J at page 23, JP-B 9-25500 and 43-4933 (herein, the term, JP-B means published Japanese Patent) and JP-A 59-19032, 59-192242 and 5-341432. In the invention, an aromatic heterocyclic mercapto compound represented by the following formula is preferred as a supersensitizer:

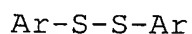


wherein M is a hydrogen atom or an alkali metal atom; Ar is an aromatic ring or condensed aromatic ring containing a nitrogen atom, oxygen atom, sulfur atom, selenium atom or tellurium atom. Such aromatic heterocyclic rings are preferably benzimidazole, naphthoimidazole, benzthiazole, naphthothiazole, benzoxazole, naphthooxazole, benzoselenazole, benzotellurazole, imidazole, oxazole, pyrazole, triazole, triazines, pyrimidine, pyridazine,



pyrazine, pyridine, purine, and quinoline. Other aromatic heterocyclic rings may also be included.

A disulfide compound which is capable of forming a mercapto compound when incorporated into a dispersion of an organic silver salt and/or a silver halide grain emulsion is also included in the invention. In particular, a preferred example thereof is a disulfide compound represented by the following formula:



wherein Ar is the same as defined in the mercapto compound represented by the formula described earlier.

The aromatic heterocyclic rings described above may be substituted with a halogen atom (e.g., Cl, Br, I), a hydroxy group, an amino group, a carboxy group, an alkyl group (having one or more carbon atoms, and preferably 1 to 4 carbon atoms) or an alkoxy group (having one or more carbon atoms, and preferably 1 to 4 carbon atoms).

In addition to the foregoing supersensitizers, a compound described in U.S. Patent No. 6,457,710, represented by the following formula (5) and a macrocyclic compound can also employed as a supersensitizer in the invention:

$$\text{H}_{31}\text{Ar} - \text{J}_{31} - \text{T}_{31} - \text{S} = \text{N}^+ \begin{matrix} \text{Ra} - \text{N} - \text{Rb} \\ \text{Rc} \\ \text{Rd} \end{matrix} \quad \left( \text{M}_{31} \right)_{\text{k}31}$$

In the formula [5], the bivalent, aliphatic hydrocarbon linkage group represented by T<sub>31</sub> include a straight-chain, branched cyclic alkylene group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms), an alkenylene group (preferably having 2 to 20 carbon atoms, more preferably 2 to

In the formula [5], the bivalent, aliphatic hydrocarbon linkage group represented by T<sub>31</sub> include a straight-chain, branched cyclic alkylene group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms), an alkenylene group (preferably having 2 to 20 carbon atoms, more preferably 2 to

16 carbon atoms, and still more preferably 2 to 12 carbon atoms), an alkynylene group (preferably having 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, and still more preferably 2 to 12 carbon atoms), each of which may be substituted by substituent group(s). The aliphatic hydrocarbon group represented by Ra, Rb, Rc, Rd, Re and Rf include, for example, an alkyl group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms and still more preferably 1 to 12 carbon atoms), an alkenyl group (preferably having 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, and still more preferably 2 to 12 carbon atoms), an alkynyl (preferably having 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, and still more preferably 2 to 12 carbon atoms) an aryl group (preferably having 6 to 30 carbon atoms, more preferably 6 to 20 carbon atoms, and still more preferably 6 to 12 carbon atoms, e.g., phenyl, naphthyl), and a heterocyclic group (e.g., 2-thiazolyl, 1-piperadynyl, 2-pyridyl, 3-pyridyl, 2-thienyl, 2-benzimidazolyl, carbazolyl, etc.). The heterocyclic group may be a monocyclic ring or a ring condensed with other ring. These groups each may be substituted at any position. Examples of such substituent groups include an alkyl group (including a cycloalkyl group and an aralkyl group, and

preferably having 1 to 20 carbon atoms, more preferably 1 to 12 carbon atoms and still more preferably 1 to 8 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, n-heptyl, n-octyl, n-decyl, n-undecyl, n-hexadecyl, cyclopropyl, cyclopentyl, cyclohexyl, benzyl, phenethyl), an alkenyl group (preferably having 2 to 20 carbon atoms, more preferably 2 to 12 carbon atoms, and still more preferably 2 to 8 carbon atoms, e.g., vinyl, allyl, 2-butenyl, 3-pentenyl, etc.), an alkynyl (preferably having 2 to 20 carbon atoms, more preferably 2 to 12 carbon atoms, and still more preferably 2 to 8 carbon atoms, e.g., propargyl, 3-pentynyl, etc.), aryl group (preferably having 6 to 30 carbon atoms, more preferably 6 to 20 carbon atoms, and still more preferably 6 to 12 carbon atoms, e.g., phenyl, p-tolyl, o-aminophenyl, naphthyl), an amino group (preferably having 0 to 20 carbon atoms, more preferably 0 to 10 carbon atoms, and still more preferably 0 to 6 carbon atoms, e.g., amino, methylamino, ethylamino, dimethylamino, diethylamino, diphenylamino, dibenzylamino, etc.), an imino group (preferably having 1 to 20 carbon atoms, more preferably 1 to 18 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., methylimino, ethylimino, propylimino, phenylimino), an alkoxy group (preferably having 1 to 20

carbon atoms, more preferably 1 to 12 carbon atoms, and still more preferably 1 to 8 carbon atoms, e.g., methoxy, ethoxy, butoxy, etc.), an aryloxy group (preferably having 6 to 20 carbon atoms, more preferably 6 to 16 carbon atoms, and still more preferably 6 to 12 carbon atoms, e.g., phenyloxy, 2-naphthyloxy, etc.), an acyl group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., acetyl, formyl, pivaloyl, benzoyl, etc.), an alkoxycarbonyl group (preferably having 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, and still more preferably 2 to 12 carbon atoms, e.g., methoxycarbonyl, ethoxycarbonyl, etc.), an aryloxycarbonyl group (preferably having 7 to 20 carbon atoms, more preferably 7 to 16 carbon atoms, and still more preferably 7 to 10 carbon atoms, e.g., phenyloxycarbonyl, etc.), an acyloxy group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 10 carbon atoms, e.g., acetoxyl, benzoyloxy, etc.), an acylamino group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 10 carbon atoms, e.g., acetylamino, benzoylamino, etc.), an alkoxycarbonylamino group (preferably having 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, and still

more preferably 2 to 12 carbon atoms, e.g., methoxycarbonylamino, etc.), an aryloxycarbonylamino group (preferably having 7 to 20 carbon atoms, more preferably 7 to 16 carbon atoms, and still more preferably 7 to 12 carbon atoms, e.g., phenyloxycarbonylamino, etc.), a sulfonylamino group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., methanesulfonylamino, benzenesulfonylamino, etc.), a sulfamoyl group (preferably having 0 to 20 carbon atoms, more preferably 0 to 16 carbon atoms, and still more preferably 0 to 12 carbon atoms, e.g., sulfamoyl, methylsulfamoyl, dimethylsulfamoyl, phenylsulfamoyl, etc.), a carbamoyl group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., carbamoyl, methylcarbamoyl, diethylcarbamoyl, phenylcarbamoyl, etc.), an alkylthio group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., methylthio, ethylthio, etc.), arylthio group (preferably having 6-20 carbon atoms, more preferably 6 to 16 carbon atoms and still more preferably 6 to 12 carbon atoms, e.g., phenylthio), an alkylsulfonyl or arylsulfonyl group

(preferably having 1 to 20 carbon atom, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., methanesulfonyl, tosyl) an alkylsulfonyl or arylsulfinyl group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., methanesulfinyl, benzenesulfinyl, etc.), an ureido group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., ureido, methylureido, phenylureido, etc.), a phosphoric acid amide group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, and still more preferably 1 to 12 carbon atoms, e.g., diethylphosphoric acid amide, phenylphosphoric acid amide, etc.), hydroxy group, mercapto group, a halogen atom (e.g., fluorine atom, chlorine atom, bromine atom, iodine atom), cyano group, sulfo group, sulfinio group, carboxy group, phosphono group, phosphono group, nitro group, hydroxamic acid group, hydrazino group, and a heterocyclic group (e.g., imidazolyl, benzimidazolyl, thiazolyl, benzothiazolyl, carbazolyl, pyridyl, furyl, piperidyl, morphoryl. etc.).

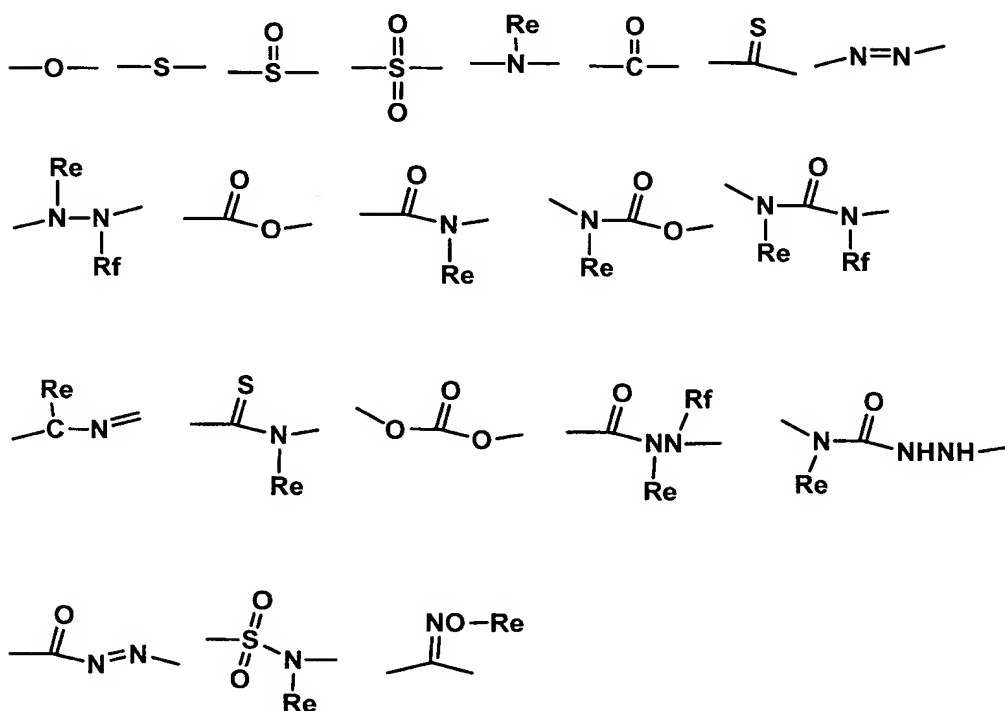
Of these substituent groups described above, hydroxy group, mercapto group, sulfo group, sulfinio group, carboxy

group, phosphono group, and phosphino group include their salts. The substituent group may be further substituted. In this case, plural substituent may be the same or different. The preferred substituent groups include an alkyl group, aralkyl group, alkoxy group, aryl group, alkylthio group, acyl group, acylamino group, imino group, sulfamoyl group, sulfonyl group, sulfonylamino group, ureido group, amino group, halogen atom, nitro group, heterocyclic group, alkoxycarbonyl group, hydroxy group, sulfo group, carbamoyl group, and carboxy group. Specifically, an alkyl group, alkoxy group, aryl group, alkylthio group, acyl group, acylamino group, imino group, sulfonylamino group, ureido group, amino group, halogen atom nitro group, heterocyclic group, alkoxycarbonyl group, hydroxy group, sulfo group, carbamoyl group and carboxy group are more preferred; and an alkyl group, alkoxy group, aryl group, alkylthio group, acylamino group, imino group, ureido group, amino group, heterocyclic group, alkoxycarbonyl group, hydroxy group, sulfo group, carbamoyl group and carboxy group are still more preferred. The amidino group include a substituted one and examples of the substituent group include an alkyl group (e.g., methyl, ethyl, pyridylmethyl, benzyl, phenethyl, carboxybenzyl, aminophenylmethyl, etc.), an aryl group (e.g.,



phenyl, p-tolyl, naphthyl, o-aminophenyl, o-methoxyphenyl, etc.), and a heterocyclic group (e.g., 2-thiazolyl, 2-pyridyl, 3-pyridyl, 2-furyl, 3-furyl, 2-thieno, 2-imidazolyl, benzothiazolyl, carbazolyl, etc.).

Examples of a bivalent linking group containing at least one of an oxygen atom, sulfur atom and nitrogen atom, represented by  $J_{31}$  include the following groups, which may be combined:



wherein Re and Rf are the same as defined in Ra through Rd.

The aromatic hydrocarbon group represented by  $ArH_{31}$  is a monocyclic or condensed aryl group (preferably having 6 to 30 carbon atoms, and more preferably 6 to 20 carbon atoms).

Examples thereof include phenyl and naphthyl, and phenyl is preferred. The aromatic heterocyclic group represented by  $\text{ArH}_{31}$  is a 5- to 10-membered unsaturated heterocyclic group containing at least one of N, O and S, which may be monocyclic or condensed with other ring. A heterocyclic ring of the heterocyclic group is preferably a 5- or 6-membered aromatic heterocyclic ring or its benzo-condensed ring, more preferably a nitrogen-containing, 5- or 6-membered aromatic heterocyclic ring or its benzo-condensed ring, and still more preferably one or two nitrogen-containing, 5- or 6-membered aromatic heterocyclic ring or its benzo-condensed ring.

Examples of the aromatic heterocyclic group include groups derived from thiophene, furan, pyrrole, imidazole, pyrazolo, pyridine, pyrazine, pyridazine, triazole, triazine, indole, indazole, purine, thiadiazole, oxadiazole, quinoline, phthalazine, naphthylizine, quinoxaline, quinazoline, cinnoline, pteridine, acrydine, phenathroline, phenazine, tetrazole, thiazole, oxazole, benzimidazole, benzoxazole, benzthiazole, benzothiazoline, benzotriazole, tetrazaindene, and carbazole. Of these, groups derived from imidazole, pyrazolo, pyridine, pyrazine, indole, indazole, thiadiazole, oxadiazole, quinoline, phenazine, tetrazole, thiazole, oxazole, benzimidazole, benzoxazole, benzthiazole,

benzothiazoline, benzotriazole, tetrazaindene, and carbazole are preferred; and groups derived from imidazole, pyridine, pyrazine, quinoline, phenazine, tetrazole, thiazole, benzoxazole, benzimidazole, benzthiazole, benzothiazoline, benzotriazole, and carbazole are more preferred.

The aromatic hydrocarbon group and aromatic heterocyclic group represented by  $\text{ArH}_{31}$  may be substituted. The substituent group is the same as the substituent groups defined in  $\text{T}_{31}$ . The substituent group may be further substituted, and plural substituting group may be the same or different. Further, the group represented by  $\text{ArH}_{31}$  is preferably an aromatic heterocyclic group.

The aliphatic hydrocarbon group represented by  $\text{Ra}$ ,  $\text{Rb}$ ,  $\text{Rc}$ ,  $\text{Rd}$ ,  $\text{Re}$  and  $\text{Rf}$  include, for example, an alkyl group (preferably having 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms and still more preferably 1 to 12 carbon atoms), an alkenyl group (preferably having 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, and still more preferably 2 to 12 carbon atoms), an alkynyl (preferably having 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, and still more preferably 2 to 12 carbon atoms) an aryl group (preferably having 6 to 30 carbon atoms, more preferably 6 to 20 carbon atoms, and still more

preferably 6 to 12 carbon atoms, e.g., phenyl, naphthyl), and a heterocyclic group (e.g., 2-thiazolyl, 1-piperadynyl, 2-pyridyl, 3-pyridyl, 2-thienyl, 2-benzimidazolyl, carbazolyl, etc.). The heterocyclic group may be a monocyclic ring or a ring condensed with other ring. The acyl group represented by Ra, Rb, Rc, Rd, Re and Rf includes an aliphatic or aromatic one, such as acetyl, benzoyl, formyl, and pivaloyl. The nitrogen containing heterocyclic group formed by combination of Ra and Rb, Rc and Rd, Ra and Rc, or Rb and Rd includes a 3- to 10-membered, saturated or unsaturated heterocyclic ring (e.g., ring groups such as piperidine ring, piperazine ring, acridine ring, pyrrolidine ring, pyrrol ring and morpholine ring).

Examples of acid anions used as the ion necessary to neutralize an intramolecular charge, represented by M<sub>31</sub> include a halide ion (e.g., chloride ion, bromide ion, iodide ion, etc.), p-toluenesulfonate ion, perchlorate ion, tetrafluoroborate ion, sulfate ion, methylsulfate ion, ethylsulfate ion, methanesulfonic acid ion and trifluoromethanesulfonic acid ion.

The supersensitizer is incorporated into the emulsion layer containing an organic silver salt and silver halide

grains, preferably in an amount of 0.001 to 1.0 mol, and more preferably 0.01 to 0.5 mol per mol of silver.

Binders suitable for photothermographic materials are transparent or translucent and generally colorless, including natural polymers, synthetic polymers or copolymers and film forming mediums. Exemplary examples thereof include gelatin, gum Arabic, polyvinyl alcohol, hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, polyvinyl pyrrolidine, casein, starch, polyacrylic acid, poly(methyl methacrylate), poly(methylmethacrylic acid), polyvinyl chloride, polymethacrylic acid, copoly(styrene-anhydrous maleic acid), copoly(styrene-acrylonitrile), copoly(styrene-butadiene), polyvinyl acetals (e.g., polyvinyl formal, polyvinyl butyral), polyesters, polyurethanes, phenoxy resin, polyvinylidene chloride, polyepoxides, polycarbonates, polyvinyl acetate, cellulose esters, and polyamides, these of which may be hydrophilic or hydrophobic.

Of these, polyvinyl acetals are preferred as a binder used for the light sensitive layer, and polyvinyl acetal is specifically preferred binder. Further, for a light insensitive layer such as an over-coating layer or a sublayer, specifically, a protective layer or a back coating layer are preferred cellulose esters exhibiting a relatively

high softening temperature, such as triacetyl cellulose and cellulose acetate-butyrate. The foregoing binders may optionally be used in combination.

The binder is used in an amount within the range effective to function as a binder. The effective range can be readily determined by one skilled in the art. As a measure to hold an organic silver salt in the light sensitive layer, the ratio by weight of a binder to an organic silver salt is preferably 15:1 to 1:2, and more preferably 8:1 to 1:1. Thus, the amount of a binder in the light sensitive elayer is preferably 1.0 to 10 g/m<sup>2</sup>. The amount of less than 1.0 g/m<sup>2</sup> results in an increase in unexposed areas, leading to levels unacceptable in practical use.

In one preferred embodiment of the invention, the photothermographic material which has been thermally developed at a temperature of 100 to 200° C, exhibits a thermal transition point of not less than 46 to 200° C. The thermal transition point is a value represented in Vicat softening point or a value represented in the ring and ball method, indicating an endothermic peak obtained when measuring the light-sensitive layer separated from the thermally developed photographic material, using a differential scanning calorimeter (or DSC, for example,

EXSTAR 6000, available from SEIKO DENSHI KOGYO Co., Ltd.; DSC 220C, SEIKO DENSHI KOGYO Co., Ltd; and DSC-7, available from Perkin Elmer Co.). In general, polymeric compounds have a glass transition point ( $T_g$ ). It was found by the inventors of the present invention that a large endothermic peak emerged at a temperature lower than the  $T_g$  value of binder resin used in the light-sensitive layer. As a result of further study of this thermal transition point temperature, it was newly found that setting the thermal transition point to a temperature of not less than 46° C and not more than 200° C prevented softening of the coating layer, thereby preventing abrasion marks.

The glass transition point ( $T_g$ ) can be determined in accordance with the method described in "Polymer Handbook" at page III-139 to III-179 (1966, published by Wiley and Sons).

In cases where the binder is a copolymer resin,  $T_g$  is defined by the following equation:

$$T_g (\text{copolymer}) = v_1 T_{g1} + v_2 T_{g2} + \cdots + v_n T_{gn}$$

where  $v_1, v_2, \cdots v_n$  each represent a weight fraction of respective monomers of the copolymer;  $T_{g1}, T_{g2}, \cdots T_{gn}$  each represent a glass transition point,  $T_g$  (°C) of a homopolymer obtained by each of monomers constituting the copolymer.

The precision of the  $T_g$  calculated by the foregoing equation is within  $\pm 5^\circ \text{C}$ .

There can be employed commonly known polymeric compounds as a binder. The glass transition point is preferably  $70$  to  $105^\circ \text{C}$ ; the number average molecular weight is preferably  $1,000$  to  $1,000,000$ , and more preferably  $10,000$  to  $500,000$ ; and the degree of polymerization is preferably  $50$  to  $1000$ . Examples thereof include compounds of a polymer or copolymer containing ethylenically unsaturated monomers as a constituting unit, such as vinyl chloride, vinyl acetate, vinyl alcohol, maleic acid, acrylic acid, acrylic acid ester, vinylidene chloride, acrylonitrile, methacrylic acid, methacrylic acid ester, styrene, butadiene, ethylene, vinyl butyral, vinyl acetal and vinyl ether; polyurethane resin, and various kinds of rubber resin. In addition thereto, phenol resin, epoxy resin, polyurethane thermally hardening type resin, urea resin, melamine resin, alkyd resin, formaldehyde resin, silicone resin, epoxy-polyamide resin, and polyester resin are also usable. These resins are detailed in "Plastic Handbook" published by Asakura-shoten. The foregoing polymeric compounds are not specifically limited and there is usable any one having a glass transition



point ( $T_g$ ) of 70 to 105° C, including homopolymers and copolymers.

Examples of polymer containing an ethylenically unsaturated monomer as a constituting unit and its copolymer include acrylic acid alkyl esters, acrylic acid aryl esters, methacrylic acid alkyl esters, methacrylic acid aryl esters, cyanoacrylic acid alkyl esters, and cyanoacrylic acid aryl esters, in which the alkyl or aryl group may be substituted. Examples of substituent groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, amyl, hexyl, cyclohexyl, benzyl, chlorobenzyl, octyl, stearyl, sulfopropyl, N-ethyl-phenylethyl,, 2-(3-phenylpropyloxy)ethyl, dimethylaminophenoxyethyl, furfuryl, tetrahydrofurfuryl, phenyl, cresyl, naphthyl, 2-hydroxyethyl, 4-hydroxybutyl, triethylene glycol, dipropylene glycol, 2-methoxyethyl, 3-methoxybutyl, 2-acetoxyethyl, 2-acetoxyacetoxyethyl, 2-ethoxyethyl, 2-iso-propoxy, 2-butoxyethyl, 2-(2-methoxy)ethyl, 2-(2-ethoxyethoxy)ethyl, 2-(2-butoxyethoxy)ethyl, 2-diphenylphosphorylethyl,  $\omega$ -methoxyethylene glycol (addition mole number  $n=6$ )allyl, and a dimethylaminoethyl chloride salt. In addition, the following monomers are also usable, including vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl

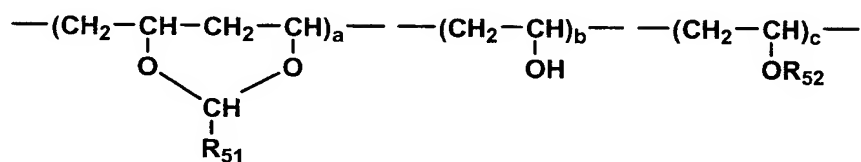
isobutyrate, vinyl caproate, vinyl chloroacetate, vinyl methoxyacetate, vinyl phenylacetate, vinyl benzoate, and vinyl salicylate; N-substituted acrylamides, N-substituted methacrylamides, acrylamides and methacrylamides, in which N-substituting groups include, for example, methyl, ethyl, propyl, butyl, tert-butyl, cyclohexyl, benzyl, hydroxymethyl, methoxyethyl, dimethylaminoethyl, phenyl, dimethyl, diethyl,  $\beta$ -cyanoethyl, N-(2-acetoacetoxyethyl) and diacetone; olefins such as dicyclopentadiene, ethylene, propylene, 1-butene, 1-pentene, vinyl chloride, vinylidene chloride, isoprene, chloroprene, butadiene, and 2,3-dimethylbutadiene; styrenes such as methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, isopropylstyrene, tert-butylstyrene, chloromethylstyrene, methoxystyrene, acetoxystyrene, chlorostyrene, dichlorostyrene, bromostyrene, and methyl vinylbenzoate; vinyl ethers such as methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, methoxyethyl vinyl ether, and dimethylaminoethyl vinyl ether; N-substituted maleimides, in which N-substituting groups include, for example, methyl, ethyl, propyl, butyl, tert-butyl, cyclohexyl, benzyl, n-dodecyl, phenyl, 2-methylphenyl, 2,6-diethylphenyl and 2-chlorophenyl; and others such as butyl crotonate, hexyl crotonate, dimethylitaconate, dibutyl itaconate, diethyl

maleate, dimethyl maleate, dibutyl maleate, diethyl fumarate, dimethyl fumarate, dibutyl fumarate, methyl vinyl ketone, phenyl vinyl ketone, methoxy ethyl ketone, glycidyl acrylate, glycidyl methacrylate, N-vinyl oxazolidone, N-vinyl pyrrolidone, acrylonitrile, methacrylonitrile, methylene malonitrile, and vinylidene chloride.

Of these polymer compounds are preferred methacrylic acid alkyl esters, methacrylic acid aryl esters and styrenes. Specifically, polymer compounds containing an acetal group are preferred, which are superior in miscibility with organic acids produced, preventing softening of the layer.

The polymer compound containing an acetal group is preferably represented by the following formula [6]:

formula [6]



wherein  $R_{51}$  is an unsubstituted or substituted alkyl group, an unsubstituted or substituted aryl group;  $R_{52}$  is an unsubstituted or substituted alkyl group, an unsubstituted or substituted aryl group,  $-COR_{53}$  or  $-COR_{53}$ , in which  $R_{53}$  is the same as defined in  $R_{51}$ .

The unsubstituted alkyl group represented by  $R_{51}$ ,  $R_{52}$  and  $R_{53}$  is preferably one having 1 to 20 carbon atoms, and more preferably 1 to 6 carbon atoms, which may be straight chain or branched, and preferably straight chain. Examples of such an unsubstituted alkyl group include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, n-amyl, t-amyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, t-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-dodecyl, and n-octadecyl. Specifically, methyl or propyl group is preferred.

The unsubstituted aryl group is preferably one having 6 to 20 carbon atoms, such as phenyl or naphthyl. Examples of a group capable of being substituted on the alkyl or aryl group include an alkyl group (e.g., methyl, n-propyl, t-amyl, t-octyl, n-nonyl, dodecyl, etc.), aryl group (e.g., phenyl), nitro group, hydroxy group, cyano group, sulfo group, alkoxy group (e.g., methoxy), aryloxy group (e.g., phenoxy), acyloxy group (e.g., acetoxy), acylamino group (e.g., acetylamino), sulfonamido group (e.g., methanesulfonamido), sulfamoyl group (e.g., methylsulfamoyl), halogen atom (e.g., fluorine, chlorine, bromine atoms), carboxy group, carbamoyl group (e.g., methylcarbamoyl), alkoxycarbonyl group (e.g., methoxycarbonyl), and sulfonyl group (e.g., methylsulfonyl). In cases where two or more substituent groups are contained,

the substituent groups may be the same or different. The total number of carbon atoms of the substituted alkyl group is preferably 1 to 20, and that of the substituted aryl group is preferably 6 to 20.

$R_{52}$  is preferably  $-\text{COR}_{53}$  (in which  $R_{53}$  is an alkyl or aryl group) or  $-\text{CONHR}_{53}$  (in which  $R_{53}$  is an aryl group); a, b and c each are the weight of respective repeating units, expressed in terms of mol%, and a is 40 to 86 mol%, b is 0 to 30 mol% and c is 0 to 60 mol%, provided that  $a+b+c=100$  mol%, a is preferably 50 to 86 mol%, b is preferably 5 to 25 mol% and c is preferably 0 to 40 mol%. The respective repeating units having composition ratio, a, b and c may be the same or different.

Polyurethane resins having commonly known structures are usable in the invention, such as polyester-polyurethane, polyether-polyurethane, polyether-polyester-polyurethane, polycarbonate-polyurethane, polyester-polycarbonate-polyurethane, and polycaprolactone-polyurethane. In the foregoing polyurethanes, at least one polar group selected from  $-\text{COOM}$ ,  $-\text{SO}_3\text{M}$ ,  $-\text{OSO}_3\text{M}$ ,  $-\text{P}=\text{O}(\text{OM})_2$ ,  $-\text{O}-\text{P}=\text{O}(\text{OM})_2$  (in which M is a hydrogen atom or an alkali metal salt),  $-\text{NR}_{54}$ ,  $-\text{N}^+\text{R}_{54}$  (in which  $R_{54}$  is a hydrocarbon group), epoxy group,  $-\text{SH}$ , and  $-\text{CN}$  is preferably introduced in

copolymerization or addition reaction. Such a polar group is preferably contained in an amount of  $10^{-8}$  to  $10^{-1}$  mol/g, and more preferably  $10^{-6}$  to  $10^{-2}$  mol/g. In addition to the polar group, it is preferred to contain at least one OH group on the end of a polyurethane molecule, i.e., at least two OH groups in total. The OH group is capable of reacting with a polyisocyanate as a hardening agent to form a three-dimensional network structure so that the more is contained in the molecule, the more preferred. Specifically, the OH group on the molecular end, which exhibits relatively high reactivity is preferred. Polyurethane having at least three OH groups (and preferably at least four OH groups) on the molecular end is preferred. Specifically, polyurethane exhibiting a glass transition point of 70 to 105° C, a rupture elongation of 100 to 2000% and a rupture stress of 0.5 to 100 N/mm<sup>2</sup> is preferred.

Polymer compounds represented by the foregoing formula (V) can be synthesized in accordance with commonly known methods, as described, for example, in "Vinyl Acetate Resin" edited by Ichiro Sakurada (KOBUNSHIKAGAKU KANKOKAI, 1962).

Other polymer compounds, as shown in Table 1 were synthesized in a similar manner. These polymer compounds may be used singly or in a blended form of at least two thereof.

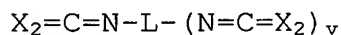
The layer containing light-sensitive silver salt (preferably, light-sensitive layer) preferably contains the foregoing polymer compounds as a main binder. The main binder refers to the state in which at least 50% by weight of the total binder of the light-sensitive silver salt-containing layer is accounted for by the foregoing polymer. Accordingly, other polymer(s) may be blended within the range of less than 50% by weight of the total binder. Such polymer(s) are not specifically limited so long as a solvent capable of dissolving the foregoing polymer is used. Examples of such polymer(s) include polyvinyl acetate, polyacryl resin and polyurethane resin.

Although it is commonly known that the use of a cross-linking agent in such a binder as described above improves layer adhesion and lessens unevenness in development, the use of the crosslinking agent is also effective in fog inhibition during storage and prevention of print-out after development.

Crosslinking agents usable in the invention include various commonly known crosslinking agents used for photographic materials, such as aldehyde type, epoxy type, vinylsulfon type, sulfonester type, acryloyl type, carbodiimide type crosslinking agents, as described in JP-A 50-96216. Of these, compounds capable of reacting with a

hydroxy group, i.e., hydroxy group-reactive compounds are preferably employed. Specifically preferred are an isocyanate type compound, epoxy compound and acid anhydride, as shown below. One of the preferred crosslinking agents is an isocyanate or thioisocyanate compound represented by the following formula [7]:

formula [7]



wherein  $v$  is 1 or 2;  $L$  is a bivalent linkage group having an alkylene, alkenylene, arylene or alkylarylene group; and  $X_2$  is an oxygen atom or a sulfur atom. The arylene ring of the arylene group may be substituted. Preferred substituents include a halogen atom (e.g., bromine atom, chlorine atom), hydroxy, amino, carboxy, alkyl and alkoxy.

The isocyanate crosslinking agent is an isocyanate compound containing at least two isocyanate group and its adduct. Examples thereof include aliphatic isocyanates, alicyclic isocyanates, benzeneisocyanates, naphthalenediisocyanates, biphenyldiisocyanates, diphenylmethandiisocyanates, triphenylmethanediisocyanates, triisocyanates, tetraisocyanates, their adducts and adducts of these isocyanates and bivalent or trivalent polyhydric



alcohols. Exemplary examples include isocyanate compounds described in JP-A 56-5535 at pages 10-12.

Specifically, adduct of isocyanate and polyhydric alcohol improves adhesion between layers, exhibiting high capability of preventing layer peeling, image slippage or production of bubbles. These polyisocyanate compounds may be incorporated into any portion of the photothermographic material, for example, into the interior of a support (e.g., into size of a paper support) or any layer on the photosensitive layer-side of the support, such as a photosensitive layer, surface protective layer, interlayer, antihalation layer or sublayer. Thus it may be incorporated into one or plurality of these layers.

The thioisocyanate type crosslinking agent usable in the invention is to be a compound having a thioisocyanate structure, corresponding to the isocyanates described above.

The crosslinking agents described above are used preferably in an amount of 0.001 to 2 mol, and more preferably 0.005 to 0.5 mol per mol of silver.

The isocyanate compounds and thioisocyanate compounds used in the invention are preferably those which are capable of functioning as a hardener. Even when "v" of formula (8)

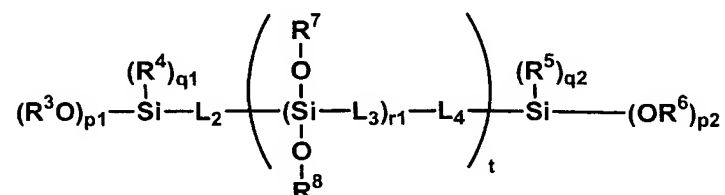
is zero, i.e., even a compound containing only one functional group provides favorable effects.

Examples of silane compounds used as a crosslinking agent include the compounds described in Japanese Patent Application No. 2000-77904, represented by the following formula (1) or (2):

formula (1)



formula (2)



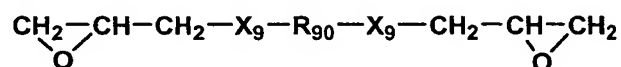
wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  represent each an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group;  $L_1$ ,  $L_2$ ,  $L_3$  and  $L_4$  represent each a bivalent linkage group;  $m$  and  $n$  are each an integer of 1 to 3, provided that  $m+n$  is 4;  $p1$  and  $p2$  are each an integer of 1 to 3 and  $q1$  and  $q2$  are each 0, 1 or 2, provided that  $p1+q1$  and  $p2+q2$  are each 3;  $r1$  and  $r2$  are each 0 or an integer of 1 to 1000; and  $x$  is 0 or 1.

In the formulas,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are each a straight chain, branched or cyclic alkyl group having

1 to 30 carbon atoms (e.g., methyl, ethyl, butyl, octyl, dodecyl, cycloalkyl, alkenyl group (e.g., propenyl, butenyl, nonanyl), an alkynyl group (e.g., acetylene group, bisacetylene group, phenylacetylene group), an aryl group (e.g., phenyl, naphthyl) or a heterocyclic group (e.g., tetrahydropyran, pyridyl group, furyl, thiophenyl, imidazolyl, thiazolyl, thiazolyl, oxadiazolyl). These groups may be substituted and the substituent groups thereof include any one of electron-withdrawing and electron-donating groups.  $L_1$ ,  $L_2$ ,  $L_3$  and  $L_4$  are each a bivalent linkage group, including an alkylene group (e.g., ethylene, propylene, butylenes, hexamethylene), oxyalkylene group (e.g., oxyethylene, oxypropylene, oxybutylene, oxyhexamethylene, or group comprised of plural these repeating units), aminoalkylene group (e.g., aminoethylene, aminopropylene, amino-hexamethylene, or a group comprised of plural these repeating units), and carboxyalkylene group (e.g., carboxyethylene, carboxypropylene, carboxybutylene), thioether group, oxyether group, sulfonamido group and carbamoyl group. At least one substituent group selected from  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  preferably is a ballast group (or a diffusion-proof group) or an adsorption-promoting group, and more preferably,  $R^2$  is a ballast group or an

The epoxy compound usable in the invention may be any one containing at least one epoxy group and is not limited with respect to the number of the epoxy group, molecular weight and other parameters. The epoxy group is preferably contained in the form of a glycidyl group through an ether bond or an imino bond in the molecule. The epoxy compound may be any one of a monomer, oligomer and polymer, in which the number of the epoxy group in the molecule is preferably 1 to 10 and more preferably 2 to 4. In cases where the epoxy compound is a polymer, it may be either one of a homopolymer and a copolymer. The number-averaged molecular weight ( $M_n$ ) thereof is preferably 2,000 to 20,000. The epoxy compound used in the invention is preferably a compound represented by the following formula [8]:

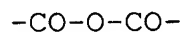
formula [8]



wherein  $R_{90}$  represents an alkylene group, and  $X_{90}$  represents a bivalent linkage group. The alkylene group represented by  $R_{90}$  may be substituted preferably by a substituent selected from a halogen atom, a hydroxyalkyl group and an amino group. The alkylene group represented by  $R_{90}$  may contain an amide linkage, ether linkage or thioether linkage; a bivalent linkage group represented by  $X$  is preferably  $-SO_2-$ ,  $-SO_2NH-$ ,  $-S-$ ,  $-O-$  or  $-NR_{91}-$ , in which  $R_{91}$  is a univalent group and preferably an electron-withdrawing group.

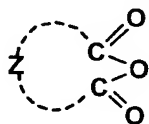
The epoxy compounds may be used alone or combination thereof. The amount to be added is not specifically limited, but preferably  $1 \times 10^{-6}$  to  $1 \times 10^{-2}$  mol/m<sup>2</sup>, and more preferably  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$  mol/m<sup>2</sup>. The epoxy compound may be added to any layer of a photosensitive layer, surface protective layer, interlayer, antihalation layer and subbing layer provided on the photosensitive layer-side of the support and may be added to one or plurality of these layers. Further, it may be added to a layer provided on the opposite side of the support, in combination with the photosensitive layer-side. In the case of a photothermographic material having photosensitive layers on both sides of the support, it may be added to any one of the layers.

The acid anhydride used in the invention is preferably a compound containing at least an acid anhydride group represented as below:



The acid anhydride usable in the invention may be any compound containing one or more acid anhydride group, the number of the acid anhydride group, molecular weight or other parameters are not specifically limited, and a compound represented by the following formula [9] is preferred:

Formula [9]



wherein Z is an atomic group necessary to form a monocyclic or polycyclic ring, which may be substituted. Examples of substituent include an alkyl group (e.g., methyl, ethyl, hexyl), an alkoxy group (e.g., methoxy, ethoxy, octyloxy), an aryl group (e.g., phenyl, naphthyl, tolyl), hydroxy group, an aryloxy group (e.g., phenoxy), an alkylthio group (e.g., methylthio, butylthio), an arylthio group (e.g., phenylthio), an acyl group (e.g., acetyl, propionyl, butyl), a sulfonyl group (e.g., methylsulfonyl, phenylsulfonyl), an acylamino group, a sulfonylamino group, an acyloxy group (e.g.,

acetoxo, benzoxy), carboxy group, cyano group, sulfo group and an amino group. It is preferred not to contain a halogen atom as a substituent.

The acid anhydride compound may be used alone or combination thereof. The amount to be added is not specifically limited, but preferably  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mol/m<sup>2</sup>, and more preferably  $1 \times 10^{-4}$  to  $1 \times 10^{-2}$  mol/m<sup>2</sup>. The acid anhydride compound may be added to any layer of a photosensitive layer, surface protective layer, interlayer, antihalation layer and subbing layer provided on the photosensitive layer-side of the support and may be added to one or plurality of these layers. Further, it may be added to a layer containing the foregoing epoxy compound.

Photothermographic imaging materials of the invention, which form photographic images on thermal development, comprises a reducible silver source (such as organic silver salts), light sensitive silver halide grains, a reducing agent, and optionally a color toning agent for adjusting silver image color tone, which are contained in the form of a dispersion in a binder matrix. Exemplary preferred toning agents are described in RD17029, U.S. Patent Nos. 4,123,282, 3,994,732, 3,846,136 and, 4,021,249. Specifically preferred

toning agents include phthalazinone, a combination of phthalazine, and phthalic acids or phthalic acid anhydrides.

With regard to image tone of the outputted image used for medical diagnosis, it has been supposed that more exact diagnostic observation results can be easily achieved with cold image tone. The cold image tone refers to pure black tone or bluish black tone and the warm image tone refers to a brownish black image exhibiting a warm tone.

The expression regarding to the tone, i.e., "colder tone" or "warmer tone can be determined based on a hue angle,  $h_{ab}$  at a density of 1.0, as defined in JIS Z 8729. The hue angle,  $h_{ab}$  can be represented as  $h_{ab} = \tan^{-1}(b^*/a^*)$  obtained from a XYZ color system, or tristimulus values X, Y and Z or  $X_{10}$ ,  $Y_{10}$  and  $Z_{10}$  defined in JIS Z 8701, using color coordinates  $a^*$  and  $b^*$  in  $L^*a^*b^*$  color system defined in JIS Z 8729. In the invention the range of the  $h_{ab}$  is  $190^\circ < h_{ab} < 260^\circ$ , preferably  $195^\circ < h_{ab} < 255^\circ$ , and more preferably  $200^\circ < h_{ab} < 250^\circ$ .

In the present invention, a matting agent is preferably incorporated into the surface layer of the photothermographic imaging material (on the light sensitive layer side or even in cases where a light insensitive layer is provided on the opposite side of the support to the light sensitive layer). In order to minimize the image abrasion after thermal



development, the matting agent is provided on the surface of a photosensitive material and the matting agent is preferably incorporated in an amount of 1 to 30% by weight of the binder.

Materials of the matting agent employed in the invention may be either organic substances or inorganic substances. Examples of the inorganic substances include silica described in Swiss Patent No. 330,158, etc.; glass powder described in French Patent No. 1,296,995, etc.; and carbonates of alkali earth metals or cadmium, zinc, etc. described in U.K. Patent No. 1,173,181, etc. Examples of the organic substances include starch described in U.S. Pat. No. 2,322,037, etc.; starch derivatives described in Belgian Patent No. 625,451, U.K. Patent No. 981,198, etc.; polyvinyl alcohols described in Japanese Patent Publication No. 44-3643, etc.; polystyrenes or polymethacrylates described in Swiss Patent No. 330,158, etc.; polyacrylonitriles described in U.S. Pat. No. 3,079,257, etc.; and polycarbonates described in U.S. Pat. No. 3,022,169.

The matting agent used in the invention preferably has an average particle diameter of 0.5 to 10  $\mu\text{m}$ , and more preferably of 1.0 to 8.0  $\mu\text{m}$ . Furthermore, the variation

coefficient of the size distribution is preferably not more than 50%, is more preferably not more than 40%, and is still more preferably not more than 30%. The variation coefficient of the grain size distribution as described herein is a value represented by the following formula:

$$\frac{(\text{standard deviation of particle size} / \text{average particle size}) \times 100}{}$$

Addition methods of the matting agent include those in which a matting agent is previously dispersed into a coating composition and is then coated, and prior to the completion of drying, a matting agent is sprayed. When plural matting agents are added, both methods may be employed in combination.

Suitable supports used in the photothermographic imaging materials of the invention include various polymeric materials, glass, wool cloth, cotton cloth, paper, and metals (such as aluminum). Flexible sheets or roll-convertible one are preferred. Examples of preferred support used in the invention include plastic resin films such as cellulose acetate film, polyester film, polyethylene terephthalate film, polyethylene naphthalate film, polyamide film, polyimide film, cellulose triacetate film and polycarbonate film, and biaxially stretched polyethylene terephthalate

(PET) film is specifically preferred. The support thickness is 50 to 300  $\mu\text{m}$ , and preferably 70 to 180  $\mu\text{m}$ .

To improve electrification properties of photothermographic imaging materials, metal oxides and/or conductive compounds such as conductive polymers may be incorporated into the constituent layer. These compounds may be incorporated into any layer and preferably into a sublayer, a backing layer, interlayer between the light sensitive layer and the sublayer. Conductive compounds described in U.S. Patent No. 5,244,773, col. 14-20.

The photothermographic material of the invention comprises at least one light-sensitive layer on the support, and further thereon, preferably having a light-insensitive layer. For example, a protective layer is provided on the light-sensitive layer. On the opposite side of the support to the light-sensitive layer, a back coating layer is preferably provided to protect the light-sensitive layer or prevent adhesion. Binders used in the protective layer or back coating layer are preferably selected from polymers which have a glass transition point higher than that of the thermally developable layer and are hard to cause abrasion or deformation, such as cellulose acetate and cellulose acetate-butylate. To adjust contrast, two or more light-sensitive

layers may be provided on one side of the support, or one or more layers may be provided on both sides of the support.

It is preferred to form a filter layer on the same side as or on the opposite side to the light sensitive layer or to allow a dye or pigment to be contained in the light sensitive layer to control the amount of wavelength distribution of light transmitted through the light sensitive layer of photothermographic imaging materials relating to the invention. Commonly known compounds having absorptions in various wavelength regions can be used as a dye, in response to spectral sensitivity of the photothermographic material. In cases where the photothermographic imaging material relating to the invention are applied as an image recording material using infrared light is preferred the use of squarilium dye containing a thiopyrylium nucleus (also called as thiopyrylium squarilium dye), squarilium dye containing a pyrylium nucleus (also called as pyrylium squarilium dye), thiopyrylium chroconium dye similar to squarilium dye or pyrylium chroconium. The compound containing a squarilium nucleus is a compound having a 1-cyclobutene-2-hydroxy-4-one in the molecular structure and the compound containing chroconium nucleus is a compound having a 1-cyclopentene-2-hydroxy,4,5-dione in the molecular structure, in which the

hydroxy group may be dissociated. Hereinafter, these dyes are collectively called a squarilium dye.

Compounds described in JP-A 8-201959 are also preferably usable as a dye.

Materials used in respective constituent layers are dissolved or dispersed in solvents to prepare coating solutions, which were coated on the support and further subjected to a heating treatment to form a photothermographic material. A coating solution for the light-sensitive layer preferably contains at least 30%, and more preferably at least 50% by weight of water. The amount of solvents are not specifically limited, but the less solvent is more preferred in terms of environment protection and it is preferred that all of solvents used are water. In one preferred embodiment of the invention, plural coating solutions are simultaneously coated to form multi-layers and then subjected to a heating treatment. Thus, coating solutions for respective constituent layers (for example, light-sensitive layer, protective layer) and coating and drying are not repeated for respective layers but plural layers are simultaneously coated and dried to form respective constituent layers. The upper layer is provided before the remaining amount of total solvents in the lower layer reaches 70% or less.

Methods for simultaneously coating plural constituent layers are not specifically limited and commonly known methods, such as a bar coating method, curtain coating method, air-knife method, hopper coating method and extrusion coating method are applicable. Of these, extrusion coating, that is, pre-measuring type coating is preferred. The extrusion coating is suitable for accurate coating of organic solvent coating since no evaporation occurs on the slide surface, as in a slide coating system. This coating method is applicable not only to the light-sensitive layer side but also to the case when simultaneously coating a backing layer with the sublayer.

The coating amount of silver is optimally selected in accordance with objectives of photothermographic materials and preferably 0.5 to 1.1.5 g/m<sup>2</sup>, more preferably 0.6 to 1.4 g/m<sup>2</sup>, and still more preferably 1.0 to 1.3 g/m<sup>2</sup>. Of the coating amount of silver described above, the amount of silver relying on silver halide accounts for preferably 2 to 18%, and more preferably 3 to 15%, based on total silver amount. The coating density of silver halide grains of at least 0.01  $\mu$ m or (circular equivalent diameter) is preferably  $1 \times 10^{14}$  to  $1 \times 10^{18}$  grains/m<sup>2</sup>, and more preferably  $1 \times 10^{15}$  to  $1 \times 10^{17}$  grains/m<sup>2</sup>. The coating density of aliphatic carboxylic acid

silver salt of at least  $0.01\text{ }\mu\text{m}$  (circular equivalent diameter) is preferably  $10^{-16}$  to  $10^{-14}$  g, and more preferably  $10^{-17}$  to  $10^{-15}$  g per silver halide grain. Coating under the condition falling the ranges described above leads to preferable results in term of the maximum silver image density per a given coating amount of silver (that is, silver covering power) and silver image tone.

The developing conditions for photographic materials are variable, depending on the instruments or apparatuses used, or the applied means and typically accompany heating the imagewise exposed photothermographic imaging material at an optimal high temperature. Latent images formed upon exposure are developed by heating the photothermographic material at an intermediate high temperature (ca.  $80$  to  $200^{\circ}\text{C}$ , and preferably  $100$  to  $200^{\circ}\text{C}$ ) over a period of ample time (generally, ca.  $1\text{ sec.}$  to ca.  $2\text{ min.}$ ). Sufficiently high image densities cannot be obtained at a temperature lower than  $80^{\circ}\text{C}$  and at a temperature higher than  $200^{\circ}\text{C}$ , the binder melts and is transferred onto the rollers, adversely affecting not only images but also transportability or the thermal processor. An oxidation reduction reaction between an organic silver salt (functioning as an oxidant) and a reducing agent is caused upon heating to form silver images.

The reaction process proceeds without supplying any processing solution such as water from the exterior.

Heating instruments, apparatuses and means include typical heating means such as a hot plate, hot iron, hot roller or a heat generator employing carbon or white titanium. In the case of a photothermographic imaging material provided with a protective layer, it is preferred to thermally process while bringing the protective layer side into contact with a heating means, in terms of homogeneous-heating, heat efficiency and working property. It is also preferred to conduct thermal processing while transporting, while bringing the protective layer side into contact with a heated roller.

Exposure of photothermographic imaging materials desirably uses a light source suitable to the spectral sensitivity of the photothermographic materials. An infrared-sensitive photothermographic material, for example, is applicable to any light source in the infrared light region but the use of an infrared semiconductor laser (780 nm, 820 nm) is preferred in terms of being relatively high power and transparent to the photothermographic material.

In the invention, exposure is preferably conducted by laser scanning exposure and various methods are applicable to



its exposure. One of the preferred embodiments is the use of a laser scanning exposure apparatus, in which scanning laser light is not exposed at an angle substantially vertical to the exposed surface of the photothermographic material. The expression "laser light is not exposed at an angle substantially vertical to the exposed surface" means that laser light is exposed preferably at an angle of  $55^{\circ}$  to  $88^{\circ}$ , more preferably  $60^{\circ}$  to  $86^{\circ}$ , still more preferably  $65^{\circ}$  to  $84^{\circ}$ , and optimally  $70^{\circ}$  to  $82^{\circ}$ . When the photothermographic material is scanned with laser light, the beam spot diameter on the surface of the photosensitive material is preferably not more than  $200\text{ }\mu\text{m}$ , and more preferably not more than  $100\text{ }\mu\text{m}$ . Thus, the smaller spot diameter preferably reduces the angle displaced from verticality of the laser incident angle. The lower limit of the beam spot diameter is  $10\text{ }\mu\text{m}$ . The thus configured laser scanning exposure can reduce deterioration in image quality due to reflected light, such as occurrence of interference fringe-like unevenness.

In the second preferred embodiment of the invention, exposure applicable in the invention is conducted preferably using a laser scanning exposure apparatus producing longitudinally multiple scanning laser light, whereby

deterioration in image quality such as occurrence of interference fringe-like unevenness is reduced, as compared to scanning laser light with longitudinally single mode. Longitudinal multiplication can be achieved by a technique of employing backing light with composing waves or a technique of high frequency overlapping. The expression "longitudinally multiple" means that the exposure wavelength is not a single wavelength. The exposure wavelength distribution is usually not less than 5 nm and not more than 10 nm. The upper limit of the exposure wavelength distribution is not specifically limited but is usually about 60 nm.

In the first, second and third preferred embodiments of the image recording method of the invention, lasers for scanning exposure used in the invention include, for example, solid-state lasers such as ruby laser, YAG laser, and glass laser; gas lasers such as He-Ne laser, Ar laser, Kr ion laser, CO<sub>2</sub> laser, Co laser, He-Cd laser, N<sub>2</sub> laser and eximer laser; semiconductor lasers such as InGa laser, AlGaAs laser, GaAsP laser, InGaAs laser, InAsP laser, CdSnP<sub>2</sub> laser, and GSe laser; chemical lasers; and dye lasers. Of these, semiconductor lasers of wavelengths of 600 to 1200 nm are preferred in terms of maintenance and the size of the light

source. When exposed onto the photothermographic imaging material in the laser imager or laser image-setter, the beam spot diameter on the exposed surface is 5 to 75  $\mu\text{m}$  as a minor axis diameter and 5 to 100  $\mu\text{m}$  as a major axis diameter. The laser scanning speed is set optimally for each photothermographic material, according to its sensitivity at the laser oscillation wavelength and the laser power.

#### **EXAMPLES**

The present invention will be further described based on examples but embodiments of the invention are by no means limited to these examples.

##### **Example 1**

###### **Preparation of Photographic Support**

On one side of blue-tinted 175  $\mu\text{m}$  thick polyethylene terephthalate film (PET) exhibiting a density of 0.170 which was previously subjected to a corona discharge treatment at 0.5  $\text{kV}\cdot\text{A}\cdot\text{min}/\text{m}^2$ , sublayer (a) was coated using the following sublayer coating solution A so as to have a dry layer thickness of 0.2  $\mu\text{m}$ . After the other side of the film was also subjected to a corona discharge treatment at 0.5  $\text{kV}\cdot\text{A}\cdot\text{min}/\text{m}^2$ , sublayer (b) was coated thereon using sublayer

coating solution B described below so as to have dry layer thickness of 0.1  $\mu\text{m}$ . Thereafter, a heating treatment was conducted at 130° C for 15 min in a heating treatment type oven having a film transport apparatus provided with plural rolls.

#### Sublayer coating solution A

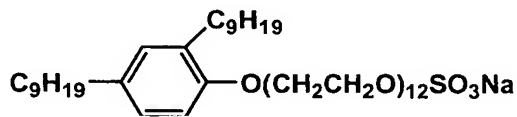
Copolymer latex solution (30% solids) of 270 g, comprised of n-butyl acrylate/t-butyl acrylate/styrene/2-hydroxyethyl acrylate (30/20/25/25%) was mixed with 0.6 g of compound (UL-1) and 0.5 g of methyl cellulose. Further thereto a dispersion in which 1.3 g of silica particles (SILOID, available from FUJI SYLYSIA Co.) was previously dispersed in 100 g of water by a ultrasonic dispersing machine, Ultrasonic Generator (available from ALEX Corp.) at a frequency of 25 kHz and 600 W for 30 min., was added and finally water was added to make 100 ml to form sub-coating solution A.

#### Sub-layer coating solution B

The foregoing colloidal tin oxide dispersion of 37.5 g was mixed with 3.7 g of copolymer latex solution (30% solids) comprised of n-butyl acrylate/t-butyl acrylate/styrene/2-hydroxyethyl acrylate (20/30/25/25%), 14.8 g of copolymer latex solution (30% solids) comprised of n-butyl

## Synthesis of colloidal tin oxide dispersion

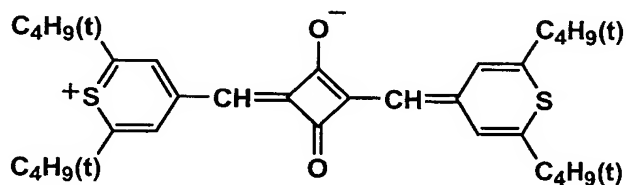
UL-1



To 830 g of methyl ethyl ketone (also denoted as MEK), 4.2 g of polyester resin (Vitel PE2200B, available from

Bostic Corp.) and 84.2 g of cellulose acetate-butyrate (CAB381-20, available from Eastman Chemical Co.) were added and dissolved. To the resulting solution were added 0.30 g of infrared dye 1, 4.5 g of fluorinated surfactant (Surflon KH40, Asahi Glass Co., Ltd.) and 2.3 g of fluorinated surfactant (Megafac F120K, Dainippon Ink Co., Ltd.) dissolved in 43.2 g of methanol were added with sufficiently stirring until being dissolved. To the resulting solution, 75 g of silica particles (SILOID 64X6000, W.R. Grace Co.) was added to prepare a coating solution for the back-layer side.

#### Infrared dye 1



The thus prepared back layer coating solution was coated on the sublayer (b) side of the support so as to form a dry thickness of 3.5  $\mu\text{m}$ , using an extrusion coater and dried at a dry bulb temperature of 100° C and a dew temperature of 10° C for 5 min.

#### Preparation of Light-sensitive Silver Halide Emulsion A

##### Solution A1

Phenylcarbamoyl gelatin	88.3 g
Compound (A) (10% methanol solution)	10 ml

Potassium bromide 0.32 g

Water to make 5429 ml

Solution B1

0.67 mol/l Aqueous silver nitrate solution

2635 ml

Solution C1

Potassium bromide 51.55 g

Potassium iodide 1.47 g

Water to make 660 ml

Solution D1

Potassium bromide 154.9 g

Potassium iodide 4.41 g

Iridium chloride (1% solution) 0.93 ml

Water to make 1982 ml

Solution E1

0.4 mol/l aqueous potassium bromide solution

Amount necessary to adjust silver potential

Solution F1

Potassium hydroxide 0.71 g

Water to make 20 ml

Solution G1

Aqueous 56% acetic acid solution 18 ml

Solution H1

Anhydrous sodium carbonate 1.72 g

Compound (A):  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n-(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_{17}-\text{CH}_2\text{CH}_2\text{O})_m\text{H}$   
( $m + n = 5$  to  $7$ )

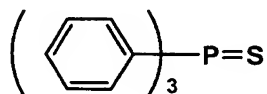
Using a stirring mixer described in JP-B Nos. 58-58288 and 58-58289, 1/4 of solution B1, the total amount of solution C1 were added to solution A1 by the double jet addition for 4 min 45 sec. to form nucleus grain, while maintaining a temperature of 45° C and a pAg of 8.09. After 1 min., the total amount of solution F1 was added thereto, while the pAg was adjusted using solution E1. After 6 min, 3/4 of solution B1 and the total amount of solution D1 were further added by the double jet addition for 14 min 15 sec., while mainlining a temperature of 45° C and a pAg of 8.09. After stirring for 5 min., the reaction mixture was lowered to 40° C and solution G1 was added thereto to coagulate the resulting silver halide emulsion. Remaining 2000 ml of precipitates, the supernatant was removed and after adding 10 lit. water with stirring, the silver halide emulsion was again coagulated. Remaining 1500 ml of precipitates, the supernatant was removed and after adding 10 lit. water with stirring, the silver halide emulsion was again coagulated. Remaining 1500 ml of precipitates, the supernatant was removed and solution H1 was added. The temperature was



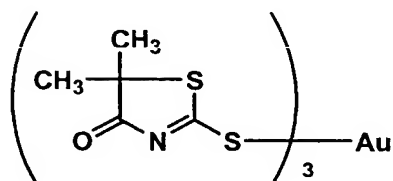
raised to 60° c and stirring continued for 120 min. Finally, the pH was adjusted to 5.8 and water was added there to so that the weight per mol of silver was 1161 g, and light-sensitive silver halide emulsion A was thus obtained. It was proved that the resulting emulsion was comprised of monodisperse silver iodobromide cubic grains having an average grain size of 0.040  $\mu\text{m}$ , a coefficient of variation of grain size of 12% and a [100] face ratio of 92%.

Next, to the foregoing emulsion, 240 ml of sulfur sensitizer S-5 (0.5% methanol solution), gold sensitizer Au-5 was further added in an amount of 1/20 molar equivalent to the sulfur sensitizer and chemical sensitization was carried out at 55° C for 120 min. The light-sensitive silver halide emulsion A was thus obtained.

S-5



Au-5



### Preparation of Powdery Organic Silver Salt

Behenic acid of 130.8 g, arachidic acid of 67.7 g, stearic acid of 43.6 g and palmitic acid of 2.3 g were dissolved in 4720 ml of water at 90° C. Then, 540.2 ml of aqueous 1.4 mol/l NaOH was added, and after further adding 6.9 ml of concentrated nitric acid, the mixture was cooled to 55° C to obtain a fatty acid sodium salt solution. To the thus obtained fatty acid sodium salt solution, 45.3 g of light-sensitive silver halide emulsion B-3 obtained above and 450 ml of water were added and stirred for 5 min., while being maintained at 55° C. Subsequently, 760 ml of 1M aqueous silver nitrate solution was added in 2 min. and stirring continued further for 20 min., then, the reaction mixture was filtered to remove aqueous soluble salts. Thereafter, washing with deionized water and filtration were repeated until the filtrate reached a conductivity of 2  $\mu$ S/cm. Using a flush jet dryer (produced by Seishin Kigyo Co., Ltd.), the thus obtained cake-like organic silver salt was dried under an atmosphere of nitrogen gas, according to the operation condition of a hot air temperature at the inlet of the dryer until reached a moisture content of 0.1% to obtain dried powdery organic silver salt A. The moisture content was measured by an infrared ray aquameter.

#### Preparation of Dispersion A

In 1457 g MEK was dissolved 14.57 g of polyvinyl butyral resin (B-79, SOLCIA Co.) and further thereto, 500 g of the foregoing powdery organic silver salt A was gradually added to obtain preliminarily dispersed mixture, dispersion A, while stirring by a dissolver type homogenizer (DISPERMAT Type CA-40M, available from VMA-GETZMANN).

#### Preparation of Light-sensitive Emulsion A

Thereafter, using a pump, the foregoing dispersion A was transferred to a media type dispersion machine (DISPERMAT Type SL-C12 EX, available from VMA-GETZMANN), which was packed 1 mm Zirconia beads (TORAY-SELAM, available from Toray Co. Ltd.) by 80%, and dispersed at a circumferential speed of 8 m/s and for 1.5 min. of a retention time with a mill to obtain light-sensitive emulsion A.

#### Preparation of Stabilizer Solution

In 4.97 g methanol were dissolved 1.0 g of Stabilizer-1 and 0.31 g of potassium acetate to obtain stabilizer solution.

#### Preparation of Infrared Sensitizing Dye Solution A

In 31.3 ml MEK were dissolved 19.2 mg of infrared sensitizing dye-1, 1.488 g of 2-chlorobenzoic acid, 2.779 g of Stabilizer-2 and 365 mg of 5-methyl-2-

mercaptobenzimidazole in a dark room to obtain an infrared sensitizing dye solution A.

#### Preparation of Additive Solution (a)

In 110 g MEK were dissolved reducing agent for silver ions, 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane (denoted as compound A, and in an amount shown in Table 1), hindered phenol (exemplified compound 3-1 in an amount shown in Table 1), 27.98 g of developer 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, 1.54 g of 4-methylphthalic acid and 0.48 g of the infrared dye 1 to obtain additive solution (a).

#### Preparation of Additive Solution (b)

Antifoggants-2, of 3.56 g were dissolved in 40.9 g MEK to obtain additive solution (b).

#### Preparation of Light-sensitive Layer Coating Solution A

Under inert gas atmosphere (97% nitrogen), 50 g of the light-sensitive emulsion A and 15.11 g of MEK were maintained at 21° C with stirring, and 390  $\mu$ m of antifoggant-1 (10% methanol solution) was added and stirred for 1 hr. Further thereto, 494  $\mu$ l of calcium bromide (10% methanol solution) was added and after stirring for 20 min. Subsequently, 1.32 g of infrared sensitizing dye solution A was added and stirred for 1 hr. Then, the mixture was cooled to 13° C and

stirred for 30 min. Further thereto, 13.31 g of polymer P-9, as binder resin was added and stirred for 30 min, while maintaining the temperature at 13° C, and 1.084 g of tetrachlorophthalic acid (9.4% MEK solution) and stirred for 15 min. Then, 12.43 g of additive solution (a), 1.6 ml of 10% MEK solution of Desmodur N3300 (aliphatic isocyanate, product by Movey Co., 10% MEK solution)) and 4.27 g of additive solution (b) were successively added with stirring to obtain coating solution A of the light-sensitive layer.

#### Preparation of Surface Protective Layer Coating Solution

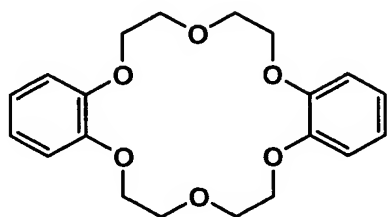
To 865 g of MEK, 96 g of cellulose acetate-butyrate (CAB171-15, available from Eastman Chemical Co.), 4.5 g of polymethyl methacrylate (Paraloid A-21, available from Rohm & Haas Corp.), 1.0 g of benzotriazole and 1.0 g of a fluorinated surfactant (EFTOP EF-105, available from JEMCO Co.) were added. Subsequently, 30 g of the foregoing matting agent dispersion was added thereto to prepare a surface protective layer coating solution.

#### Preparation of Matting Agent Dispersion

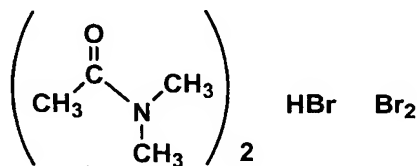
To 42.5 g of MEK, 7.5 g of cellulose acetate-butyrate (CAB171-15, available from Eastman Chemical Co.) was added with stirring. Further thereto, 5 g of Silica particles

(SYLOID 320, available from FUJI SYLYSIA Co.) was added and stirred a for 30 min. to obtain a matting agent dispersion.

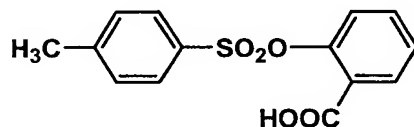
Stabilizer 1



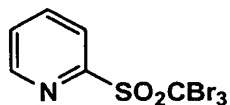
Antifoggant 1



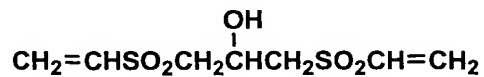
Stabilizer 2



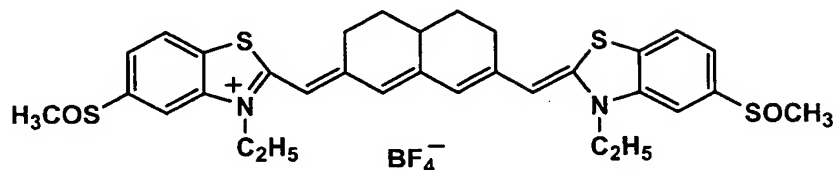
Antifoggant 2



VSC



Infrared sensitizing dye 1



#### Preparation of Sample No. 101

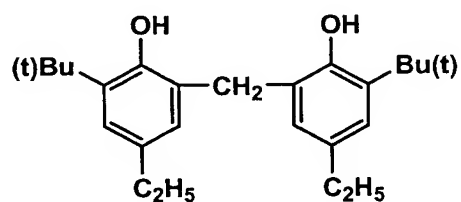
The light-sensitive layer coating solution A and the surface protective layer coating solution were simultaneously coated on the sublayer (a) of the support using an extrusion coater. Coating was conducted so as to form a light-sensitive layer having a silver coverage of  $1.5 \text{ g/m}^2$  and a  $2.5 \text{ }\mu\text{m}$  thick surface protective layer. Drying was carried out for 10 min with hot air of a dry bulb temperature of  $75^\circ \text{C}$  and a dew point of  $10^\circ \text{C}$ . Sample No. 101 was thus obtained.

Samples No. 102 through 120 were each coated similarly to Sample No. 101, provided that the reducing agent and hindered phenol in the light-sensitive layer coating solution A [i.e., reducing agent and hindered phenol in the additive solution (a)] were each replaced by compound shown in Table 1.

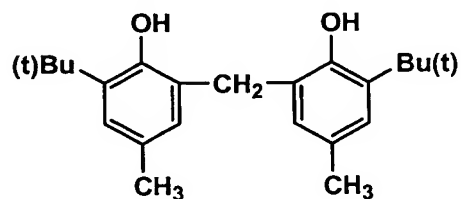
Table 1

Sample No.	Reducing Agent ( $\alpha$ ) ( $10^{-3}$ mol/m <sup>2</sup> )	Hindered Phenol ( $\beta$ ) ( $10^{-5}$ mol/m <sup>2</sup> )	$\beta/\alpha$ (molar ratio)	Remark
101	A (3.0)	3-1 (3.0)	0.01	Comp.
102	Comp-1 (3.0)	3-1 (3.0)	0.01	Comp.
103	Comp-2 (3.0)	3-1 (3.0)	0.01	Comp.
104	Comp-3 (3.0)	3-1 (3.0)	0.01	Comp.
105	1-1 (3.0)	3-1 (3.0)	0.01	Inv.
106	1-7 (3.0)	3-1 (3.0)	0.01	Inv.
107	1-9 (3.0)	3-1 (3.0)	0.01	Inv.
108	1-15 (3.0)	3-1 (3.0)	0.01	Inv.
109	1-40 (3.0)	3-1 (3.0)	0.01	Inv.
110	1-43 (3.0)	3-1 (3.0)	0.01	Inv.
111	1-43 (3.0)	3-1 (0.15)	0.0005	Inv.
112	1-44 (3.0)	3-1 (3.0)	0.01	Inv.
113	1-44 (3.0)	2-8 (90.0)	0.30	Inv.
114	1-44 (3.0)	3-5 (3.0)	0.01	Inv.
115	1-45 (2.4)	3-1 (3.0)	0.01	Inv.
116	1-45 (2.4)	2-10 (120.0)	0.40	Inv.
117	1-48 (3.0)	3-1 (0.15)	0.0005	Inv.
118	1-52 (3.0)	3-1 (6.0)	0.02	Inv.
119	1-64 (2.4)	3-1 (120.0)	0.40	Inv.
120	1-64 (2.4)	3-5 (3.0)	0.01	Inv.

Comparative compound 1 (Comp-1)

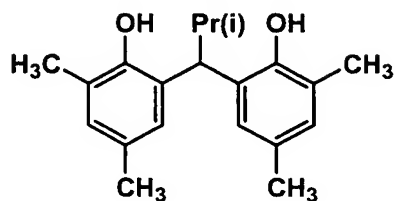


Comparative compound 2 (Comp-2)





## Comparative compound 3 (Comp-3)



## Exposure and Processing

Samples each were subjected to laser scanning exposure from the emulsion side using an exposure apparatus having a light source of 800 nm and 814 nm semiconductor laser of longitudinal multi-mode, which was made by means of high frequency overlapping. In this case, exposure was conducted at an angle of 75°, between the exposed surface and exposing laser light and as a result, images with superior sharpness were unexpectedly obtained, as compared to exposure at an angle of 90°. Subsequently, using an automatic processor provided with a heated drum, exposed samples were subjected to thermal development at a temperature of 110 °C for 15 sec., while bringing the protective layer surface of the photothermographic material into contact with the drum surface. Exposure and thermal development were conducted in an atmosphere at 23° C and 50% RH. Obtained images were evaluated based on densitometry.

## Evaluation of Characteristics

The thus processed samples were evaluated with respect to obtained images according to the following procedure.

#### Sensitivity, Fog Density and Maximum Density

Processed samples were each subjected to densitometry using a Macbeth densitometer (TD-904) to prepare a characteristic curve comprised of abscissa (exposure) and ordinate (density). Sensitivity (also designated  $S$ ) was represented by the reciprocal of exposure giving a density of 1.0 above the density of an unexposed area (minimum density), based on the sensitivity of sample No. 101 being 100. The minimum (or fog density, designated  $D_{\min}$ ) and maximum density (designated  $D_{\max}$ ) were also determined. Sensitivity and maximum density were each represented by a relative value, based on those of Sample No. 101 exposed with 810 nm semiconductor laser being 100.

#### Hue Angle ( $h_{ab}$ )

The hue angle ( $h_{ab}$ ) was determined in the manner that processed samples were measured with respect to areas corresponding to the minimum density and an optical density of 1.0 using a colorimetric light source, D65 of CIE and a spectral colormeter CM-508d (available from Minolta Co., Ltd.) at a visual field of  $2^\circ$ .

#### Evaluation of Image Lasting Quality

Thermally processed samples were measure with respect to image lasting quality, based on variation in minimum density and maximum density to evaluate image lasting quality, in accordance with the following procedure.

#### Variation in Minimum Density

Samples which were thermally processed similarly to the foregoing sensitometry were continuously exposed to light in an atmosphere at 45° C and 55% RH for 3 days, in which commercially available white fluorescent lamp was arranged so as to exhibit an illumination intensity of 500 lux on the surface of each sample. Thereafter, exposed and unexposed samples were measured for the minimum density, and variation in fog density was determined in accordance with the following equation:

$$\text{Variation in minimum density} = (D_2 - D_1) / D_1 \times 100 (\%).$$

wherein  $D_1$  represents the minimum density of a sample unexposed to fluorescent lamp light and  $D_2$  represents the minimum density of a sample exposed to fluorescent lamp light. A value closer to 100 indicates a superior result.

#### Variation in Maximum Density

Thermally developed samples were prepared similarly to the determination of variation in fog density. After being allowed to stand under the environment of 25° C or 45° C for

3 days, maximum densities after being allowed to stand were measured and variation in image density was determined as a measure of image lasting quality, in accordance with the following equation:

$$\text{Variation in maximum density} = (\text{maximum density of sample aged at } 45^{\circ} \text{ C}) / (\text{maximum density of sample aged at } 25^{\circ} \text{ C}) \times 100 (\%)$$

#### Hue Angle of Aged Image

Processed samples obtained by exposure to 810 nm semiconductor laser were aged at 45 °C and 55% RH for 3 days while being irradiated by a commercially available white fluorescent lamp at an illumination intensity of 500 Lux on the sample surface. Thereafter, the hue angle ( $h_{ab}$ ) was measured in the manner that processed samples were measured with respect to areas corresponding to the minimum density and an optical density of 1.0, using a colorimetric light source, D65 of CIE and a spectral colorimeter CM-508d (available from Minolta Co., Ltd.) at a visual field of 2°.

The thus obtained results are shown in Table 2.

Table 2

Sample No.	Unaged Sample						Image Lasting Quality (810 nm)				Remark
	Fog (810 nm)	Sensitivity		D <sub>max</sub>		h <sub>ab</sub> (810 nm)	D <sub>min</sub> (%)	D <sub>max</sub> (%)	h <sub>ab</sub>		
		810 nm	814 nm	810 nm	814 nm						
101	0.220	100	80	100	80	190	150	85	160	Comp.	
102	0.230	105	80	100	79	190	155	80	160	Comp.	
103	0.245	105	80	100	80	190	155	75	165	Comp.	
104	0.245	105	82	100	82	190	160	75	150	Comp.	
105	0.195	115	99	115	110	210	107	96	210	Inv.	
106	0.190	117	110	117	110	215	107	95	210	Inv.	
107	0.195	115	110	115	110	210	106	96	210	Inv.	
108	0.200	115	109	115	108	255	106	95	250	Inv.	
109	0.195	115	108	115	110	250	102	95	245	Inv.	
110	0.175	120	119	120	119	250	102	95	245	Inv.	
111	0.180	120	115	120	110	210	101	92	210	Inv.	
112	0.170	125	120	125	121	250	101	96	250	Inv.	
113	0.185	120	111	115	105	270	101	90	270	Inv.	
114	0.190	115	107	115	111	255	102	96	260	Inv.	
115	0.200	135	127	130	127	260	102	96	260	Inv.	
116	0.200	120	117	120	110	270	101	90	270	Inv.	
117	0.180	120	107	117	105	210	102	91	210	Inv.	
118	0.180	120	117	120	115	255	101	97	245	Inv.	
119	0.195	130	118	110	105	270	101	90	270	Inv.	
120	0.195	135	129	117	115	245	101	98	240	Inv.	

As can be seen from Table 2, it was shown that inventive photothermographic material samples exhibited enhanced sensitivity, relatively high maximum density and improved fogging, resulting in minimized deterioration in images (maximum density, fogging) after being kept under light or heating and leading to stabilized sensitivity and maximum density of the outputted images even when exposed using a laser scanning exposure apparatus at different oscillating wavelengths (810 nm, 814nm). It was also proved that the inventive samples resulted in images exhibited a hue angle ( $h_{ab}$ , defined in CIE) falling within the range of more than  $180^\circ$  and less than  $270^\circ$  and having cold-tone and improved resistance to light or heat, thereby outputting images suitable for diagnosis.